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Journal of Research

of the

National Bureau of Standards

Vol. 31, No. 6 December 1943

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Journal of Research

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Volume 31, Number 6
December 1943

[Published with the approval of the Director of the Budget]

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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1567

Part of Journal of Research of the National Bureau of Standards, Volume 31, December 1943

pH VALUES OF ACID-SALT MIXTURES OF SOME AROMATIC SULFONIC ACIDS AT VARIOUS TEMPERATURES AND A CRITERION OF COMPLETENESS OF DISSOCIATION

By Walter J. Hamer, Gladys D. Pinching, and S. F. Acree

ABSTRACT

A method is described to differentiate between completely and incompletely dissociated acids by means of measurements of the emf of galvanic cells without liquid junctions. Hydrogen and silver-silver-chloride electrodes and solutions of the acid, its sodium or potassium salt, and sodium or potassium chloride are used. The activity coefficients of hydrochloric acid in such mixtures are calculated by the equation relating the emf to the activity of hydrochloric acid in known concentrations of the acid and salts. If the mean values of the activity coefficient of hydrochloric acid in the mixtures are higher than those predicted by the limiting law of Debye and Hückel, the acid is then considered to be completely dissociated. If they are lower, the acid is incompletely dissociated. By this method it was found that the sulfonic acid group in *p*-phenolsulfonic and 4-chlorophenol-2-sulfonic acids may be regarded as completely dissociated into sulfonate and hydrogen ions at temperatures of 10°, 25°, 40°, and 60° C.

Solutions containing *p*-phenolsulfonic acid, its sodium or potassium salt, and sodium or potassium chloride and solutions containing 4-chlorophenol-2-sulfonic acid, its sodium salt, and sodium chloride are suitable for use as pH standards. Their pH values range from 1.2 to 2.5 and vary only slightly with temperature changes. Directions for their preparation are given.

The significance of the complete dissociation of the sulfonic acid group in the calculation of the ionization constants and pH values of sulfonate buffers and indicators is discussed in terms of the tautomeric relations and the theory of color changes of indicators.

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I. INTRODUCTION

In measurements of acidity, knowledge of the degree of dissociation of a sulfonic acid group in indicators or buffers is important. Wingfield and Acree [1][1] have reported that the changes in the molar absorption index of β-naphthoquinonesulfonic acid upon the addition of different amounts of hydrochloric acid and various salts can best be

[1] Figures in brackets indicate the literature references at the end of this paper.

interpreted by assuming that the sulfonic acid group is almost completely dissociated into ions. However, their attempts to determine the degree of dissociation of the sulfonic acid from pH measurements with a glass electrode and a saturated calomel half-cell involved a number of uncertainties and led to the conclusion that β-naphthoquinonesulfonic acid might have an ionization constant as low as 0.03 to 0.10. On the other hand, conductivity measurements indicate that sulfonic acids are completely dissociated. This inconsistency may be attributed partly to the neglect of corrections for the potential of the liquid junction between the solutions of sulfonic acid and saturated potassium chloride of the calomel half-cell. Hamer and Acree [2] have shown that values of the ionization constants of weak acids determined from cells with liquid junction may be in error by as much as 46 percent, depending upon the method used to estimate the values of the liquid-junction potentials. Errors would be even greater for acids of large ionization constants [3]. Additional uncertainties may be attributed to salt errors of the glass electrode. This electrode was employed because β-naphthoquinonesulfonic acid is readily reduced at a hydrogen electrode.

As the above methods are complicated, it is the purpose of this report to describe a procedure using galvanic cells without liquid junction for determining whether the dissociation of strong acids is essentially complete. The method is illustrated by data on *p*-phenolsulfonic and 4-chlorophenol-2-sulfonic acids. These acids were chosen because they are not reduced at the hydrogen electrode; are obtained in a fair state of purity; may be used as pH standards for the two pH ranges covered by the sulfonic and phenolic groups; have a structure similar to those of many indicators; and give spectrophotometric curves resembling those of sulfonphthalein indicators in the ultraviolet.

II. TAUTOMERIC EQUILIBRIA OF PHENOL-SULFONIC ACIDS

In order to determine the pH values of sulfonphthalein indicators and *p*-phenolsulfonate buffers, it is necessary to know the ionization constants of their sulfonic acid and phenolic groups. Both ionization constants must be determined by means of a mass-action equation, including the activities of the hydrogen and organic ions obtained by potentiometric, spectrophotometric, or other methods. The expressions involving tautomeric equilibria must also be considered, since the evidence so far obtained from spectrophotometric data, alkylation reactions, and pH measurements indicates that the free acids and salts of the above indicators and buffers must be treated as tautomeric compounds, such as are illustrated in figure 1.

The mathematical methods for correlating dissociation and equilibrium constants of tautomers have already been developed [4, 5, 6]. The fractional transformation, α, of the indicator or buffer into bivalent ions, and the change in color,[2] with increase in neutralization with alkali and corresponding rise in pH are represented by eq 1,

[2] The *p*-phenolsulfonates and indicators give absorption index bands in the ultraviolet that are as different for acid and alkaline solutions as are the visible bands for indicators. The molar absorption indices are used as a measure of the concentrations of the molecules and ions of these organic compounds [6, 8, 9]. The equations apply regardless of the number of uni- and bivalent electromers or electronic states giving the corresponding index bands [5, p. 220].

which is a simplification of the general equations governing such tautomeric compounds [4, 6].

$$H\alpha/(1-\alpha)=[K_{1Q}K_{2Q}R+K_{1P}K_{2P}]/[(K_{1P}+H)+R(K_{1Q}+H)]. \quad (1)$$

In eq 1 the apparent ionization and equilibrium constants are the classical ones and contain terms for the activity coefficients for each reaction shown in figure 1; α is the sum of the concentrations of the resonant bivalent ions ($P^{=}+Q^{=}$) obtained from the data for the absorption indices or otherwise; and H is the hydrogen-ion concentration. This equation is similar in form to those for dibasic acids having no tautomeric properties.

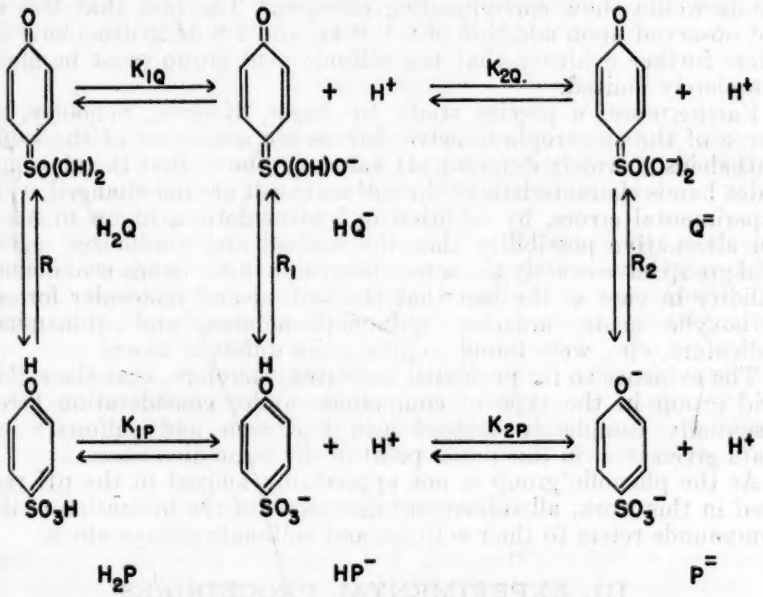

FIGURE 1.—*Tautomeric and electromeric forms of p-phenolsulfonates*

H_2Q, HQ^-, and $Q^=$ represent the molecular, univalent, and bivalent forms of the quinoidal structure.
H_2P, HP^-, and $P^=$ represent the molecular, univalent, and bivalent phenolic structures.
R, R_1, and R_2 represent the ratios H_2Q/H_2P, HQ^-/HP^-, and $Q^=/P^=$.
K_{1Q} and K_{2Q} represent the primary and secondary ionization constants of the quinoidal form.
K_{1P} and K_{2P} represent the primary and secondary ionization constants of the phenolic form.

The apparent ionization constants and ionization relations of the phenol and sulfonic acid groups in sulfonphthaleins and phenolsulfonates are thus very complex in that they involve activity coefficients and several equilibrium and ionization constants. The value of $H\alpha/(1-\alpha)$ for any given hydrogen-ion concentration depends greatly on the relative magnitudes of the first and second ionization constants. If the sulfonic acid group is almost completely ionized under all conditions, as usually assumed for strong mineral acids and bases, and K_{1P}/K_{2P} and K_{1Q}/K_{2Q}, therefore large, eq 1 reduces to eq 2

$$H\alpha/(1-\alpha)=K_2, \quad (2)$$

which is the form for the second ionization constant of *p*-phenol-

sulfonates and sulfonphthalein indicators, involving only the dissociation of the phenolic group, as follows:

$$SO_3^-ROH \rightleftharpoons SO_3^-RO^- + H^+.$$

Use of the mass law (eq 2) and emf data by Bates, Siegel, and Acree [7], including the corresponding values of the activity coefficients of the ions, gave a good second ionization constant for phenolsulfonic acid. Practically the same value was obtained by Sager, Schooley, and Acree by spectrophotometric methods [8]. If the sulfonic acid group were incompletely ionized, however, more of its molecules would be formed upon the addition of a strong acid to either the sulfonate salt or the free sulfonic acid, and the spectral absorption bands would show corresponding changes. The fact that this was not observed upon addition of 0.1, 0.44, and 1.9 *M* hydrochloric acid offers further evidence that the sulfonic acid group must be almost completely ionized.

Furthermore, a precise study by Sager, Keegan, Schooley, and Acree of the spectrophotometric curves for a number of the sulfonphthaleins at widely different pH values [9] shows that the absorption index bands characteristic of the sulfonate salt are not changed, within experimental errors, by addition of hydrochloric acid up to 0.5 *M*. An alternative possibility that the ionized and nonionized sulfonic acid group have exactly the same absorption index bands is of doubtful validity in view of the fact that the ionized and molceular forms of carboxylic acids, urazoles, quinonephenolates, and quinaminone indicators, etc., were found to give quite different bands.

The evidence so far presented indicates, therefore, that the sulfonic acid group in the type of compounds under consideration here is essentially completely ionized into hydrogen and sulfonate ions. Data given later in this paper point in the same direction.

As the phenolic group is not appreciably ionized in the pH range used in this work, all subsequent discussion of the ionization of these compounds refers to their sulfonic and sulfonate groups alone.

III. EXPERIMENTAL PROCEDURES

1. MATERIALS

Sodium *p*-phenolsulfonate obtained from a commercial source was recrystallized four times from distilled water and dried to constant weight at 105° C. The purity of the material was found to be 98 percent by bromometric assay [7, 8]. The original sample contained traces of sulfate and phenol, which were absent in the purified material. Impurities in the recrystallized material are probably cresol sulfonate and phenoldisulfonate. In the pH range 1.2 to 2.5 used in the work neither of these impurities could affect the conclusions.

Potassium *p*-phenolsulfonate obtained from a commercial source was dissolved in distilled water, treated three times with activated carbon to remove colored impurities, recrystallized four times from distilled water, and dried at 110° C. By bromometric assay it was

found to have a purity of 100.1 percent. Differential titration with carbonate-free sodium hydroxide [7] indicated a purity of 100.1 percent. Both methods of assay have an estimated uncertainty of 0.1 percent.

Sodium 4-chlorophenol-2-sulfonate obtained from a commercial source was dissolved in distilled water, digested with four successive portions of activated carbon to remove colored impurities, recrystallized twice from distilled water, and dried at 105° C. Whereas the original material contained traces of sulfate, the purified material was found to be free of this impurity.

The hydrochloric acid solution was prepared by dissolving hydrogen chloride gas in conductivity water [10]. The strength of the acid was determined by weight titration with a standardized solution of carbonate-free sodium hydroxide, using phenolphthalein as the indicator. Determinations agreed within 0.05 percent.

2. SOLUTIONS

Stock solutions were prepared from a known weight of the dry sodium or potassium salt and the requisite weight of hydrochloric acid. The more dilute solutions were prepared from known weights of stock solution and conductivity water.

Three different stock solutions containing different ratios of acid to salt were used for the measurements on *p*-phenolsulfonic acid. One contained equal molal quantities of sodium *p*-phenolsulfonate, *p*-phenolsulfonic acid, and sodium chloride. A second contained the same constituents in the ratio of 3:1:3. In the third, the potassium salts were used in the corresponding ratio of 5:2:5. For the measurements on 4-chlorophenol-2-sulfonic acid, only one stock solution containing sodium 4-chlorophenol-2-sulfonate, 4-chlorophenol-2-sulfonic acid, and sodium chloride in the ratio 1:1:1 was employed.

3. APPARATUS AND METHOD

Galvanic cells with hydrogen and silver-silver-chloride electrodes were employed. These cells are of the type used in this Bureau in work on pH standards and have been described in previous papers [3, 11, 12]. Measurements were made at 10°, 25°, 40°, and 60° C in order to determine the effect of temperature upon the degree of dissociation of the acids. Solutions containing mixtures of the acid, its sodium or potassium salts, and sodium or potassium chloride were employed rather than solutions of the pure acids alone. The addition of the chloride is a prerequisite for the use of the silver-silver-chloride electrode in such mixtures.

The details of the apparatus employed in this investigation, including the cells, bubble tubes, electrodes, thermostat, and the emf recording instruments, have been described by Hamer and Acree [12]. The cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled within 0.01° C at the four temperatures, and the emf was measured by means of a calibrated potentiometer with galvanometer and standard cell.

IV. ELECTROMOTIVE-FORCE MEASUREMENTS

The galvanic cell employed for these measurements may be represented by

$$\mathrm{Pt,\ H_2(g)|HAn}(m_1),\ \mathrm{MAn}(m_2),\ \mathrm{MCl}(m_3)|\mathrm{AgCl(s)|Ag(s)}.$$

An designates the sulfonate anion, and M represents either sodium or potassium. Molality was chosen as the concentration unit.

The emf of this cell at a pressure of 1 atmosphere of hydrogen is given by

$$E=E^\circ-\frac{RT}{F}\ln(a_{\mathrm{H}}a_{\mathrm{Cl}})=E^\circ-\frac{RT}{F}\ln(f_{\mathrm{H}}f_{\mathrm{Cl}}m_{\mathrm{H}}m_{\mathrm{Cl}}), \quad (1)$$

in which E is the measured emf in international volts; E° is the potential of the silver–silver-chloride electrode in international volts for unit activity of hydrochloric acid; a, m, and f represent, respectively, the activity, molality, and activity coefficient of the ionic species denoted by subscripts; and R, T, and F have their usual significance.

TABLE 1.—*Electromotive force of the galvanic cell* $\mathrm{Pt,\ H_2(g)|HAn}(m_1),\ \mathrm{MAn}(m_2),\ \mathrm{MCl}(m_3)|\mathrm{AgCl(s)|Ag}$ *at 10°, 25°, 40°, and 60° C*

Concentrations of solutions in moles of solutes per 1,000 g of water		emf in volts at—			
$m_1=m_3$	m_2	10° C	25° C	40° C	60° C
Mixtures of 4-chlorophenol-2-sulfonic acid, the sodium salt and sodium chloride					
0.10093	0.10094	0.35790	0.35597	0.35288	0.34724
.07513	.07514	.37164	.37036	.36801	.36302
.05147	.05147	.38902	.38866	.38703	.38347
.02569	.02569	.42080	.42203	.42204	.42055
.009676	.009676	.46421	.46754	.46936	.47009
.008138	.008138	.47240	.47615	.47806	.47928
.006236	.006236	.48430	.48867	.49166	.49440
.004343	.004343	.50171	.50702	.51117	.51511
Mixtures of *p*-phenolsulfonic acid, the sodium salt and sodium chloride					
0.10090	0.09552	0.35732	0.35540	0.35244	0.34699
.06862	.06497	.37543	.37437	.37225	.36799
.05057	.04787	.38962	.38929	.38790	.38448
.03490	.03304	.40697	.40751	.40700	.40465
.009558	.009049	.46604	.46943	.47179	.47314
.007992	.007566	.47453	.47849	.48120	.48335
.10093	.03366	.35677	.35476	.35177	.34628
.06271	.02092	.37871	.37798	.37591	.37160
.04389	.014637	.39536	.39534	.39419	.39104
.024710	.008240	.42188	.42310	.42339	.42203
.009350	.003118	.46650	.46976	.47167	.47372
.008496	.002833	.47086	.47441	.47651	.47900
.006449	.002151	.48382	.48796	.49112	.49427
.004350	.001451	.50277	.50777	.51184	.51689
Mixtures of *p*-phenolsulfonic acid, the potassium salt and potassium chloride					
0.10093	0.04070	0.35739	0.35547	0.35245	0.34675
.05870	.02367	.38241	.38170	.37994	.37582
.04216	.01700	.39752	.39763	.39661	.39353
.02926	.01180	.41415	.41500	.41481	.41271
.010018	.004040	.46338	.46676	.46896	.47021
.008320	.003355	.47176	.47546	.47799	.47975
.006217	.002507	.48524	.48969	.49292	.49562
.003990	.001609	.50649	.51192	.51652	.52090

In table 1 values of the observed emf corrected to unit hydrogen pressure in the usual manner [13] are given for the temperatures of 10°, 25°, 40°, and 60° C and for the various solutions of concentrations recorded in columns 2 and 3. After each experiment the solutions were withdrawn from the cells and analyzed for *p*-phenolsulfonic acid by the bromate method and tested for sulfinic acid, a possible reduction product, by the addition of dilute potassium permanganate. The sulfonate concentrations of all the solutions agreed with their original values within 0.2 percent and sulfinic acid was not detected. The steadiness of the emf over a considerable time period was also evidence that no reduction of the sulfonates had occurred. The values of the emf recorded are the average of duplicate measurements, all of which agreed within 0.10 millivolt.

V. DISSOCIATION OF *p*-PHENOLSULFONIC AND 4-CHLOROPHENOL-2-SULFONIC ACIDS

It is well known that the determination of ionization constants of the order of 0.01 to 0.10 is a complicated procedure and involves several successive approximations for the determination of the hydrogen-ion concentration [11]. A briefer and more direct method was devised to circumvent these extensive calculations. According to eq 1, the emf of the galvanic cell is a function of known constants $E°$, R, T, and F, and the unknown quantities m and f. Upon rearrangement, eq 1 becomes

$$\frac{E-E°}{2.3026RT/F}+\log(m_{H}m_{Cl})=-\log(f_{H}f_{Cl}) \tag{2}$$

or

$$J=-\log(f_{H}f_{Cl})=-2\log f_{\pm} \tag{3}$$

where

$$J \text{ equals } (E-E°)/(2.3026RT/F)+\log(m_{H}m_{Cl}), \text{ and } f_{\pm}$$

denotes the mean activity coefficient. If it is assumed that the acid and salts are completely dissociated into ions, values of $J/2$ can be calculated, which give the mean activity coefficients of hydrochloric acid in the mixtures studied. Furthermore, by making this assumption, the values of $J/2$ must be similar to those for acids and salts which are completely dissociated into ions, and will be higher than those predicted by the limiting law of Debye and Hückel [14]. On the other hand, if the values of $J/2$ do not conform to those for a completely dissociated acid or salt, it will then be necessary to revert to the more complicated method of successive approximations in order to determine the degree of dissociation of the acids or salts. To illustrate, values of $J/2$ were calculated from data given in the literature for a typical strong electrolyte (hydrochloric acid) and for a number of typical weak electrolytes which were investigated by a similar type of galvanic cell, using the values of $E°$ determined by Harned and Ehlers [15] and the numerical values of R, T, and F given in a previous report [11]. Values of $J/2$ at 25° C for hydrochloric acid, the bisulfate ion ($K=0.0120$) formic acid ($K=1.772\times10^{-4}$), acetic acid ($K=1.754\times10^{-5}$), and malonic acid (second step in its ionization) ($K=2.014\times10^{-6}$) obtained respectively by Harned and Ehlers [15], Hamer [16], Harned

and Embree [17], Harned and Ehlers [18], and Hamer, Burton and Acree [11] are shown plotted in figure 2 as functions of the square root of the ionic strength. The dotted line (curve C) corresponds to the theoretical values of $J/2$ predicted by the limiting law of Debye and Hückel. The data for hydrochloric acid fall above the dotted line, whereas the data for the weak acids (curves D, E, F, and G) fall below the dotted line. The weaker the acid, the farther are its values of $J/2$ below the dotted line. In other words, the activity coefficients of those acids or salts which are completely dissociated into ions are greater than those predicted by the Debye-Hückel equation, whereas those

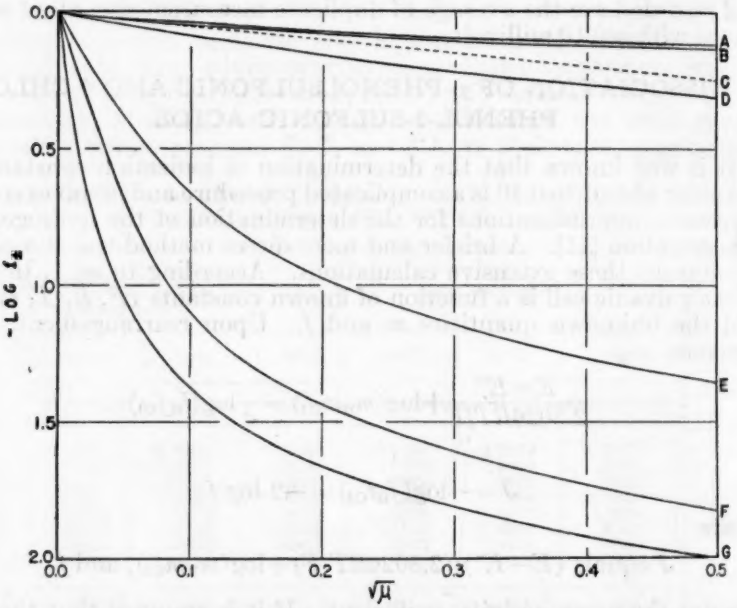

FIGURE 2.—*Plots of the negative of the common logarithm of the mean activity coefficient of hydrochloric acid, or values of $J/2$, in solutions of various acid-salt mixtures against the square root of the ionic strength at 25° C.*

A, Hydrochloric acid; *B*, sulfonate-acid mixtures; *C*, values calculated by means of the limiting law of Debye and Hückel; *D*, sodium acid sulfate-hydrochloric acid mixtures; *E*, sodium formate-hydrochloric acid mixtures; *F*, sodium acetate-hydrochloric acid mixtures; and *G*, disodium malonate-hydrochloric acid mixtures.

which are incompletely dissociated into ions are lower. Values of $J/2$ obtained for the sulfonate mixtures investigated in this work are given in table 2 and are shown plotted as curve B in figure 2 at 25° C. All the data for the different sulfonate solutions lie on curve B within the limits of the scale used in constructing this figure. These values, like pure hydrochloric acid, fall above the dotted line. On the basis of this criterion, it follows that the sulfonic acid groups are completely dissociated into ions. In figure 3 the data for the three different *p*-phenolsulfonate solutions are shown plotted with respect to the square root of the ionic strength at 10°, 25°, 40°, and 60° C. The data all fall above those for the limiting law (straight line) and hence *p*-phenolsulfonic acid is completely dissociated at the four temperatures. In figure 4, similar data are plotted for 4-chlorophenol-2-

sulfonic acid mixtures. Obviously, similar conclusions regarding complete dissociation for these mixtures may be made.

TABLE 2.—*Activity coefficient of hydrochloric acid in sulfonate solutions at 10°, 25°, 40°, and 60° C*

Concentrations of solutions in moles of solutes per 1,000 g of water		Activity coefficients at—							
HCl	Salt	10° C		25° C		40° C		60° C	
		obs.	calc.*	obs.	calc.*	obs.	calc.*	obs.	calc.*
Mixtures of 4-chlorophenol-2-sulfonic acid, the sodium salt and sodium chloride									
0.10093	0.20187	0.740	0.739	0.735	0.736	0.728	0.728	0.713	0.713
.07513	.15027	.750	.749	.747	.745	.739	.738	.727	.724
.05147	.10294	.766	.766	.763	.766	.759	.755	.744	.743
.02589	.05138	.800	.803	.799	.803	.794	.794	.781	.784
.009676	.019352	.873	.856	.874	.853	.877	.849	.875	.842
.008138	.016275	.877	.865	.879	.862	.888	.858	.886	.852
.006236	.012472	.897	.878	.899	.875	.900	.872	.889	.866
.004343	.008686	.901	.894	.903	.892	.900	.889	.889	.884
Mixtures of *p*-phenolsulfonic acid, the sodium salt and sodium chloride									
0.10090	0.19642	0.749	0.742	0.744	0.742	0.735	0.734	0.716	0.716
.06862	.13359	.759	.755	.756	.753	.748	.746	.731	.731
.05057	.09844	.770	.768	.767	.766	.760	.760	.744	.747
.03490	.06794	.782	.788	.780	.785	.773	.779	.758	.768
.009558	.018607	.851	.858	.853	.856	.849	.852	.840	.845
.007992	.015557	.855	.867	.855	.865	.853	.861	.840	.855
.10093	.13459	.757	.749	.753	.748	.744	.731	.725	.725
.06271	.08363	.777	.769	.771	.767	.765	.761	.751	.748
.04389	.05853	.789	.788	.786	.785	.779	.779	.764	.768
.02471	.03295	.814	.820	.813	.817	.805	.812	.791	.803
.009350	.012469	.862	.871	.866	.868	.870	.865	.850	.859
.008496	.011329	.867	.875	.871	.873	.875	.869	.853	.864
.006449	.008600	.876	.888	.881	.886	.879	.882	.861	.877
.004350	.005801	.880	.904	.888	.902	.888	.899	.861	.895
Mixtures of *p*-phenolsulfonic acid, the potassium salt and potassium chloride									
0.10093	0.14163	0.748	0.748	0.743	0.747	0.734	0.740	0.719	0.724
.05870	.08237	.770	.771	.766	.769	.759	.762	.745	.750
.04216	.05916	.786	.788	.782	.786	.775	.780	.762	.769
.02926	.04106	.805	.808	.804	.806	.797	.800	.786	.791
.010018	.014058	.857	.866	.857	.863	.854	.860	.843	.854
.008320	.011675	.869	.875	.871	.873	.869	.869	.860	.863
.006217	.008724	.883	.888	.884	.886	.882	.883	.872	.878
.003990	.005599	.890	.907	.894	.905	.888	.902	.875	.898

* Calculated by eq 4.

The values of $J/2$ or $-\log f_{\pm}$ recorded in the tables vary with the ionic strength in a manner typical of strong electrolytes. This variation may be represented by the Hückel extension [19] of the Debye-Hückel equation for univalent ions, namely,

$$-1/2 \log(f_H f_{Cl}) = -\log f_{\pm} = \frac{A\sqrt{\mu}}{1+Ba_1\sqrt{\mu}} + \beta\mu, \qquad (4)$$

where A and B are constants whose numerical values depend upon various natural constants, β is an empirical constant expressing in part the interactions of the nonpolar hydrogen and chloride ions with

the polar phenolsulfonate ions [8, 9, 32] analogous to Kirkwood's treatment of ampholytes [20], a_1 is the so-called closest distance of approach of the ions; and μ is the ionic strength of the mixtures. Molality was used as the concentration unit in this equation, following the suggestion of Scatchard [21]. Values of a_1 and β were determined for each series in the usual manner by substituting two measured values of $-\log f_{\pm}$ and their corresponding ionic strengths in the above equation and then solving the two simultaneous equations for the unknowns. It was found that the best value for a_1 was 3.5 A for the four series and that β has values at the temperatures of 10°, 25°, 40°,

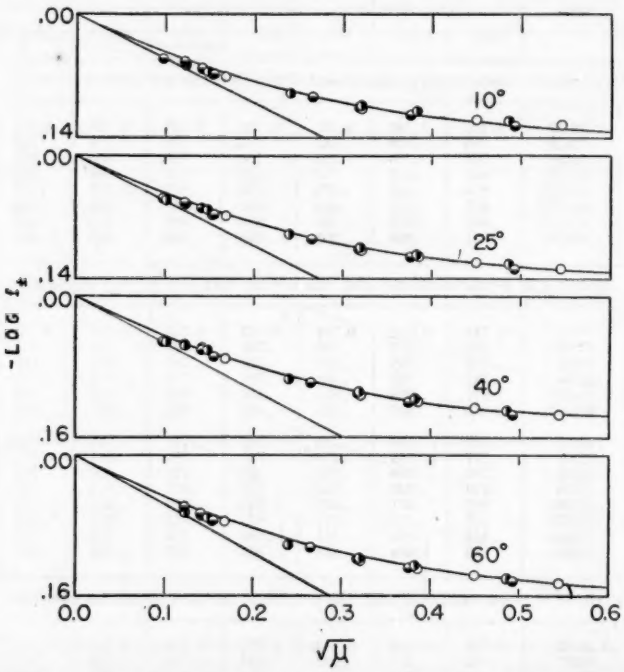

FIGURE 3.—*Plots of the negative of the common logarithm of the mean activity coefficient of hydrochloric acid, or values of $J/2$, in solutions of sodium and potassium p-phenolsulfate, sodium and potassium chloride, and p-phenolsulfonic acid against the square root of the ionic strength.*

○, ◑, and ◒ represent, respectively, values of 2:1, 4:3, and 7:5 for the ratio of sulfonate concentration to hydrochloric acid concentration. The curved line represents the calculated values and the straight line corresponds to the values given by the limiting law of Debye and Hückel.

and 60°, respectively, of 0.121, 0.126, 0.127, and 0.117 for 4-chlorophenol-2-sulfonic acid and 0.125, 0.137, 0.137, and 0.124 for p-phenolsulfonic acid. Values of $-\log f_{\pm}$ calculated by eq 4 are given in table 2. At all the temperatures, the calculated and observed values of $-\log \pm f_{\pm}$ agree with a mean deviation of ± 0.002 for the concentrated and ± 0.023 for the most dilute solutions of the 4-chlorophenol-2-sulfonate series, and ± 0.006 for all the concentrations of the sodium and potassium *p*-phenolsulfonate series. It is apparent, however, that a smooth curve drawn through the observed values for the most dilute solutions of the *p*-phenolsulfonates would be slightly concave toward the axis of abscissas. Robinson [22] observed a similar be-

havior for pure salts of sulfonic acids, which may be attributed in part to the presence of "ion pairs" arising from the resonant, polar structure of the phenolsulfonates [8, 9, 32]. The value of a_1 found here is nearly equal to Bjerrum's [23] critical value and may indicate, although not conclusively, that "ion pairs" are present. Their presence, however, does not alter the conclusion that these sulfonic acids are almost completely dissociated into hydrogen and sulfonate ions, since "ion pairs" result from electrostatic forces.

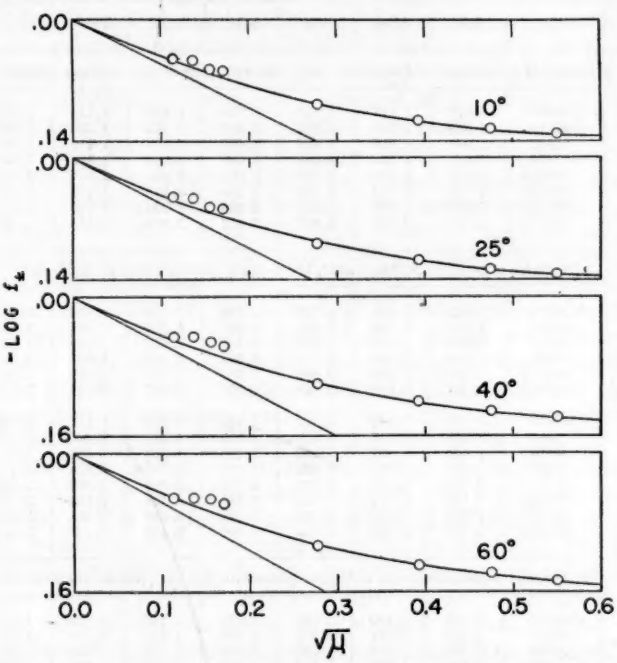

FIGURE 4.—*Plots of the negative of the common logarithm of the mean activity coefficient of hydrochloric acid, or values of J/2, in solutions of sodium 4-chlorophenol-2-sulfonate, sodium chloride and 4-chlorophenol-2-sulfonic acid against the square root of the ionic strength.*

Circles represent the experimental values, the curved line represents the calculated values, and the straight line corresponds to the values given by the limiting law of Debye and Hückel.

VI. CALCULATIONS OF THE pH VALUES OF THE ACID-SALT MIXTURES

The pH value of a solution is defined as the common logarithm of the reciprocal of the hydrogen ion activity, expressed by the equation

$$\mathrm{pH} = -\log a_{\mathrm{H}} = -\log(m_{\mathrm{H}} f_{\mathrm{H}}). \qquad (5)$$

In section V, values of $f_\pm$ for the acid-salt mixtures were given. With the assumption that $f_{\mathrm{H}} = f_\pm$ in these mixtures, it is possible to calculate their pH values. They were computed at the four temperatures by using both the experimental and calculated values of the mean activity coefficients and the known values of the hydrogen-ion concentrations (i. e., of the hydrochloric acid) in these mixtures and are given in table 3. The pH values computed from the experimental

and calculated values of the activity coefficients agree within ±0.004 at the four temperatures.

TABLE 3.—pH *values of sulfonate solutions at 10°, 25°, 40°, and 60° C*

Concentrations of solutions in moles of solutes per 1,000 g of water		pH values at—							
		10° C		25° C		40° C		60° C	
$m_1 = m_3$	m_2	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Mixtures of 4-chlorophenol-2-sulfonic acid, the sodium salt and sodium chloride									
0.10093	0.10094	1.127	1.127	1.129	1.129	1.134	1.134	1.143	1.143
.07513	.07514	1.249	1.250	1.251	1.252	1.255	1.256	1.262	1.264
.05147	.05147	1.404	1.404	1.406	1.404	1.408	1.410	1.417	1.417
.02569	.02569	1.687	1.686	1.688	1.686	1.690	1.691	1.698	1.696
.009676	.009676	2.073	2.082	2.073	2.083	2.071	2.085	2.072	2.089
.008138	.008138	2.146	2.152	2.146	2.154	2.141	2.156	2.142	2.159
.006236	.006236	2.252	2.262	2.251	2.263	2.251	2.265	2.256	2.267
.004343	.004343	2.407	2.411	2.407	2.412	2.408	2.413	2.413	2.416
Mixtures of *p*-phenolsulfonic acid, the sodium salt and sodium chloride									
0.10090	0.09552	1.122	1.126	1.125	1.126	1.130	1.130	1.141	1.141
.06862	.06497	1.283	1.286	1.285	1.287	1.289	1.291	1.300	1.299
.05057	.04787	1.409	1.411	1.411	1.412	1.415	1.416	1.425	1.423
.03490	.03304	1.564	1.561	1.565	1.562	1.569	1.566	1.577	1.572
.009558	.009049	2.090	2.086	2.089	2.087	2.091	2.089	2.096	2.093
.007992	.007566	2.165	2.159	2.165	2.161	2.167	2.162	2.173	2.166
.10093	.03366	1.117	1.122	1.119	1.122	1.125	1.127	1.136	1.136
.06271	.02092	1.312	1.317	1.316	1.318	1.319	1.322	1.327	1.329
.04389	.01464	1.460	1.461	1.462	1.463	1.466	1.466	1.474	1.472
.02471	.008240	1.697	1.693	1.697	1.695	1.701	1.698	1.709	1.702
.009350	.003118	2.094	2.089	2.091	2.091	2.090	2.092	2.100	2.095
.008496	.002833	2.133	2.129	2.131	2.130	2.129	2.132	2.140	2.134
.006449	.002151	2.248	2.242	2.245	2.243	2.246	2.245	2.255	2.247
.004350	.001451	2.417	2.405	2.413	2.406	2.413	2.407	2.427	2.410
Mixtures of *p*-phenolsulfonic acid, the potassium salt and potassium chloride									
0.10093	0.04070	1.122	1.122	1.125	1.123	1.130	1.127	1.139	1.136
.05870	.02367	1.345	1.344	1.347	1.346	1.351	1.349	1.359	1.356
.04216	.01700	1.480	1.478	1.482	1.480	1.486	1.483	1.493	1.489
.02926	.01180	1.628	1.626	1.629	1.628	1.632	1.630	1.638	1.636
.010018	.004040	2.063	2.062	2.066	2.063	2.068	2.065	2.073	2.068
.008320	.003355	2.141	2.138	2.140	2.139	2.141	2.141	2.146	2.144
.006217	.002507	2.259	2.258	2.260	2.259	2.261	2.261	2.266	2.263
.003990	.001609	2.450	2.442	2.448	2.443	2.451	2.444	2.457	2.446

Although these solutions do not have as large a buffer capacity as do solutions prepared from a weak acid and its salt, they do have a slight buffer capacity, of approximately the same magnitude as hydrochloric acid–sodium chloride mixtures [24] frequently used for the same range of pH. When a solution containing 2 parts of sodium chloride and 1 part of hydrochloric acid is diluted from an ionic strength of 0.3 to 0.03, it shows a change in pH of +0.933. A change of +0.924 occurs for a similar dilution of a solution containing 2 parts of sodium 4-chlorophenol-2-sulfonate and 1 part of hydrochloric acid, and a change of +0.933 occurs for a similar dilution of a solution containing 2 parts of sodium *p*-phenolsulfonate and 1 part of hydrochloric acid.

The pH values of these solutions increase linearly with the temperature at a rate of 0.00025 to 0.00045 pH unit per degree, depending upon the concentration. This variation is in accord with the general behavior of buffer solutions in that the pH of solutions of low pH

increases with a rise in temperature and decreases for solutions of high pH [25, 26]. They are therefore very suitable for use as pH standards.

VII. DISCUSSION

The conclusion that the sulfonic acid groups in *p*-phenolsulfonic and 4-chlorophenol-2-sulfonic acids are completely dissociated into hydrogen and sulfonate ions in solutions of an ionic strength of 0.3 or less and at temperatures of 10°, 25°, 40°, and 60° C agrees with results obtained by electrical conductivity and spectrophotometric measurements. It may be concluded that the same group in indicators of similar structure will likewise be completely dissociated in dilute solutions, a conclusion previously arrived at by Wingfield and Acree [1]. An extension of this conclusion to more complex compounds must be made with caution, however, since sulfonic acids of large molecular weight have a tendency to exhibit colloidal characteristics. Although the results of conductivity measurements on a series of straight-chain sulfonic acids [27] show that the sulfonic acid group is completely dissociated, they also indicate that there is a gradual transition from typically strong electrolytes to well-marked colloidal electrolytes consisting of "ion micelles" as the number of carbon atoms increases from 2 to 14, with heptyl and nonyl acids occupying an intermediate position. A similar study of a series of aromatic sulfonic acids [28] also indicates the complete dissociation of the sulfonic acid group but a smaller tendency to form ion micelles than for straight-chain sulfonic acids containing the same number of carbon atoms. Another series of measurements indicates that halogen substitution in the ring increases slightly the tendency to form ion micelles [29]. The critical concentration at which ion micelles first appear is generally very low and may be as small as 0.0004 *N* [30]. This critical concentration is also greatly decreased on the addition of neutral salts [31]. Hence in most cases ion micelles may be present in very dilute solutions of complex sulfonic acids, especially after addition of large concentrations of salts. The optical properties of solutions of less complex phenolsulfonate buffers and of sulfonaphthalein indicators show that the presence of ion micelles is highly improbable. Nevertheless, cognizance must be taken of their possible existence in the presentation of data on theories and use of indicators as pH standards.

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WASHINGTON, October 22, 1943.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1568

Part of Journal of Research of the National Bureau of Standards, Volume 31, December 1943

AXIAL RIGIDITY OF PERFORATED STRUCTURAL MEMBERS

By Martin Greenspan

ABSTRACT

Formulas are derived for computing the over-all lengthening (or shortening) of a tension (or compression) member having a uniform gross cross section and a series of similar perforations of circular, elliptical, or "ovaloid" shape uniformly distributed along the length.

Tests made on strips having circular perforations show that the applicable formula gives good results over the practical range of the variables.

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I. INTRODUCTION

The work reported in this paper is part of an investigation at the National Bureau of Standards on perforated cover plates. The results of tests on a large number of columns having perforated cover plates have been reported [1].[1] From these results may be computed a value for each perforated column of an "axial rigidity factor", K, which is the ratio of the axial rigidity of the column to the axial rigidity of an

[1] Figures in brackets indicate the literature references at the end of this paper.

unperforated, but otherwise similar, column. The axial rigidity, R, of a tension or compression member of length L is defined from

$$e=\frac{PL}{R},$$

where P is the axial load and e the lengthening or shortening of the member, and P/e is constant. For a member of uniform cross-sectional area A_g, $R=EA_g$, where E is Young's modulus of elasticity.

In this paper are derived formulas for computing the axial-rigidity factor of a member having a uniform gross cross section and a series of similar perforations of circular, elliptical, or "ovaloid" shape uniformly distributed along the length. Such formulas may find application whenever information concerning displacements in a structure having perforated members is required. Examples are the analysis of indeterminate structures and the computation of the camber of trusses.

The results of some tests on tension members having circular perforations are reported and compared with the values computed from the applicable formula.

II. A REDUCTION OF THE PROBLEM

Consider a long tension (or compression) member of uniform gross cross section, containing a series of similar perforations spaced uniformly along the length. The member is supposed subjected to an axial load, P, and it is desired to study the over-all deformation in the axial direction produced by the load.

For this purpose the member is considered divided into similar bays of length $2l$, each bay containing one perforation. If the perforation has symmetry about an axis perpendicular to that of the tension member, the analysis may be confined to a half-bay of length l. The problem is now to determine the over-all extension of the half-bay when subjected to a load, P, distributed over the net area, A_n, on one end, and over the gross area, A_g, on the other end, in such a manner that these ends remain plane (fig. 1, a).

With the x-axis taken parallel to the outer elements of the member, and the origin of coordinates on the transverse axis of the perforation, the problem is to find the displacement, u_l, of the end $x=l$, that of the end $x=0$ being taken as zero. The x-components of the displacements of points on the bounding surface of the perforation will be denoted by u_p.

Consider, in addition, a state of stress in the member consisting of a uniform normal stress $\sigma_x=P/A_g$ throughout, all other stresses being zero (fig. 1, b). This stress could be maintained by surface loads $\pm P/A_g$ per unit of projected (on the yz-plane) area, positive on the right end and negative on the left end, of the member. The displacement of the end $x=l$ is Pl/A_gE.

To these two states of stress, namely (a) that prevailing in the original problem, and (b) that characterized by a uniform stress, the reciprocal theorem [2] may be applied. This theorem states that the work done by the external forces which correspond to the first state acting through the displacements which correspond to the second state is equal to the work done by the external forces which corre-

[2] See p. 173 of reference [2].

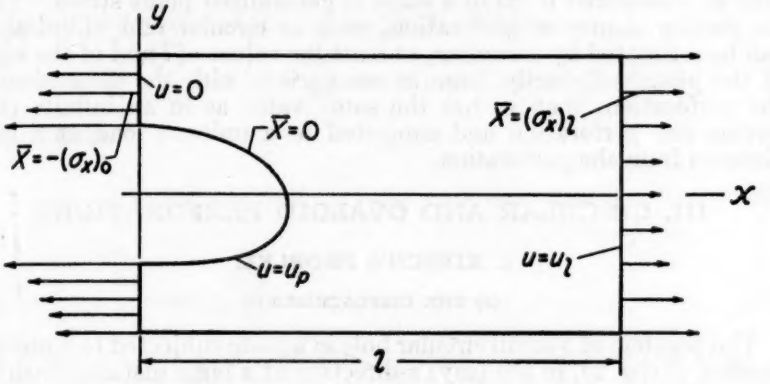
spond to the second state acting through the displacements which correspond to the first state. Hence

$$\frac{1}{2}Pu_1-\frac{1}{2}\int\frac{P}{A_g}u_x dydz=\frac{1}{2}\frac{P^2l}{A_gE},$$

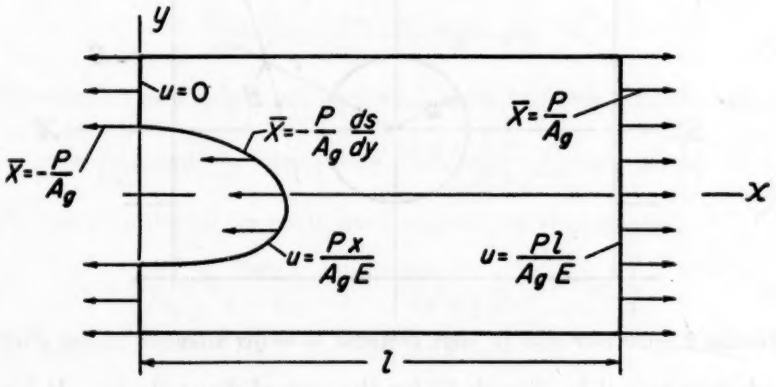
or

$$u_1=\frac{Pl}{A_gE}+\frac{1}{A_g}\int u_x dydz, \tag{1}$$

where the integration is to be taken over the projection on the yz-plane of the bounding surface of the perforation.



(a)



(b)

FIGURE 1.—*Two states of stress in a half-bay of the member.*

(a) The cross sections $x=0$ and $x=l$ remain plane; (b) uniform stress, in the axial direction, throughout.

In an unperforated member of the same gross dimensions and subjected to the same load as the perforated half-bay, the displacement, u'_1, of the end $x=l$ is

$$u'_1=\frac{Pl}{A_gE}.$$

The ratio of the axial rigidity of the perforated member to that of the unperforated member is the same as the ratio of these displacements. Hence

$$K=\frac{u'_l}{u_l}=\frac{1}{1+\frac{E}{Pl}\int u_p dydz}. \tag{2}$$

Equation 2 enables the computation of K, provided the values of u_p can be determined. If the problem be restricted to the case where the perforation occurs in a relatively thin plate of constant thickness, t, then the material in the neighborhood of the perforation may be considered to be in a state of generalized plane stress. Then for certain shapes of perforation, such as circular and elliptical, u_p can be estimated by assuming, at least for values of l and of the width of the plate sufficiently large in comparison with the dimensions of the perforation, that u_p has the same value as in an infinite plate having one perforation and subjected to a uniform load at a large distance from the perforation.

III. CIRCULAR AND OVALOID PERFORATIONS

1. KIRSCH'S PROBLEM

(a) THE DISPLACEMENTS

The problem of a small circular hole in a plate subjected to a uniform tension, S (fig. 2), in the (say) x-direction at a large distance from the

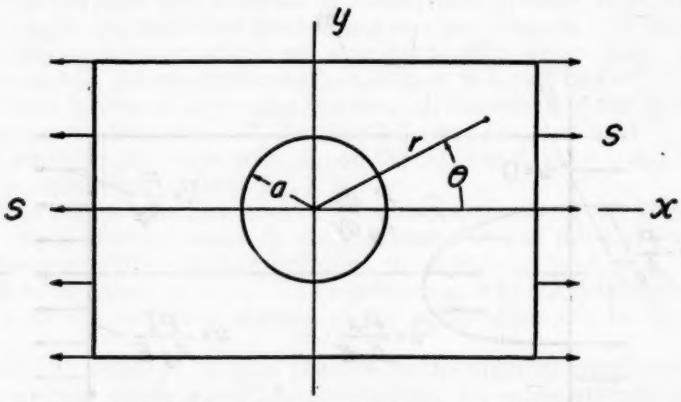


FIGURE 2.—*Circular hole in plate subjected to uniform tension in one direction.*

hole was solved by Kirsch [3] for the case of plane strain. It is convenient to solve for the displacements in the case of plane stress by a method[3] depending on a knowledge of the Airy stress function, ϕ. The function, ψ, defined, in the absence of body forces, by

$$\frac{\partial^2\psi}{\partial x\partial y}=\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}=\nabla^2\phi,$$

with ψ adjusted by means of the arbitrary functions of integration (of

[3] See p. 130 of reference [4].

the form $f_1(x)+f_2(y)$), so that $\nabla^2\psi=0$, is called the displacement function. The x-component of the displacement is given by

$$u=\frac{1}{E}\left[\frac{\partial\psi}{\partial y}-(1+\nu)\frac{\partial\phi}{\partial x}\right], \tag{3}$$

where ν is Poisson's ratio.

The solution to Kirsch's problem is given by the stress function [4]

$$\phi=\frac{S}{4}\left[r^2-2a^2\log r-\frac{(r^2-a^2)^2}{r^2}\cos 2\theta\right], \tag{4}$$

where a is the radius of the circle (fig. 2), so that

$$\nabla^2\phi=\frac{\partial^2\psi}{\partial x\partial y}=S\left(1-\frac{2a^2}{r^2}\cos 2\theta\right)=S\left[1-2a^2\frac{x^2-y^2}{(x^2+y^2)^2}\right].$$

From which

$$\frac{\psi}{S}=xy-2a^2\tan^{-1}\frac{x}{y}+c(x^2-y^2)+dx+ey+f, \tag{5}$$

and

$$\frac{1}{S}\frac{\partial\psi}{\partial y}=x+\frac{2a^2x}{x^2+y^2}-2cy+e. \tag{6}$$

The primitive of ψ is harmonic, so that the arbitrary functions of integration represented by the last four terms in eq 5 are merely the most general harmonic function of the form $f_1(x)+f_2(y)$.

From eq 4

$$\frac{\partial\phi}{\partial x}=\frac{S}{2}a^2x\frac{x^2+y^2-a^2}{(x^2+y^2)^3}(3y^2-x^2). \tag{7}$$

Substitution of $\partial\psi/\partial y$ from eq 6 and $\partial\phi/\partial x$ from eq 7 in eq 3 gives

$$u=\frac{S}{E}\left[x+\frac{2a^2x}{x^2+y^2}-2cy+e-\frac{1+\nu}{2}a^2x\frac{x^2+y^2-a^2}{(x^2+y^2)^3}(3y^2-x^2)\right].$$

The condition $u=0$ for $x=0$ gives $c=e=0$, so that finally,

$$u=\frac{S}{E}\left[x+\frac{2a^2x}{x^2+y^2}-\frac{1+\nu}{2}a^2x\frac{x^2+y^2-a^2}{(x^2+y^2)^3}(3y^2-x^2)\right]. \tag{8}$$

For points on the circle $x^2+y^2=a^2$, eq 8 becomes

$$u_p=\frac{3Sx}{E}. \tag{9}$$

Equation 9 gives the value of u_p that should be used in eq 2 to obtain K.

(b) THE LOAD

It remains to determine the value of P in eq 2. Consider the strip bounded by the lines $y=\pm na$. If t is the thickness of the plate, the

[4] See p. 484 of reference [4].

total load carried by the strip is $P'=2\int_0^{na}\sigma_x t dy$. This load is a function of x/a, and will vary along the length of the strip from $x=a$ to $x=l$. However, this variation is small for sufficiently large n, as is easily shown. From eq 4

$$\sigma_x=\frac{\partial^2\phi}{\partial y^2}=S\left[1-\frac{5a^2}{2(x^2+y^2)}+\frac{a^2(2y^2+3a^2)}{2(x^2+y^2)^2}\right.$$
$$\left.-\frac{4a^2y^2(2y^2+3a^2)}{(x^2+y^2)^3}+\frac{12a^4y^4}{(x^2+y^2)^4}\right],$$

and with the notation, $x=ma$,

$$P'=2\int_0^{na}\sigma_x t dy=2Snat\left[1-\frac{1}{2(m^2+n^2)}-\frac{4m^2+1}{2(m^2+n^2)^2}+\frac{2m^2}{(m^2+n^2)^3}\right]. \quad (10)$$

From eq 10 it may be computed that for given n, $P'/2Snat$ will vary from its value at $m=0$ by not more than 2 percent for the following values of n and m:

$n=3$,	$m\not>6$
$n=4$,	$m\not>13$
$n\geqslant 5$,	any m.

Hence P' may be taken as its value at $m=0$, that is, as the load transmitted by the strip across the minimum cross section, or

$$P'=2Snat\left(1-\frac{1}{2n^2}-\frac{1}{2n^4}\right).$$

P' may be used for P in eq 2 if n be interpreted as

$$A_g/2at=\frac{A_g}{A_g-A_n};$$

hence

$$P=SA_g\left(1-\frac{1}{2n^2}-\frac{1}{2n^4}\right)=SA_gC(n), \quad (11)$$

say. $C(n)$ may be considered to be a correction factor depending on n.

2. AXIAL RIGIDITY FOR CIRCULAR PERFORATIONS

Substitution of u_p from eq 9 and P from eq 11 in eq 2 gives

$$K=\frac{1}{1+\frac{3}{C(n)}\frac{1}{A_gl}\int xtdy}.$$

The integral above is one-half of V_0 the volume of the perforation, and A_gl is one-half of V_g, the gross volume of one bay of the tension member. Hence

$$K=\frac{1}{1+\frac{3}{C(n)}\frac{V_0}{V_g}}. \tag{12}$$

3. AXIAL RIGIDITY FOR OVALOID PERFORATIONS

An "ovaloid" perforation is one having the shape of a rectangle with a semicircle erected on each end. Consider a tension member having an ovaloid perforation with dimensions as shown in figure 3 and with

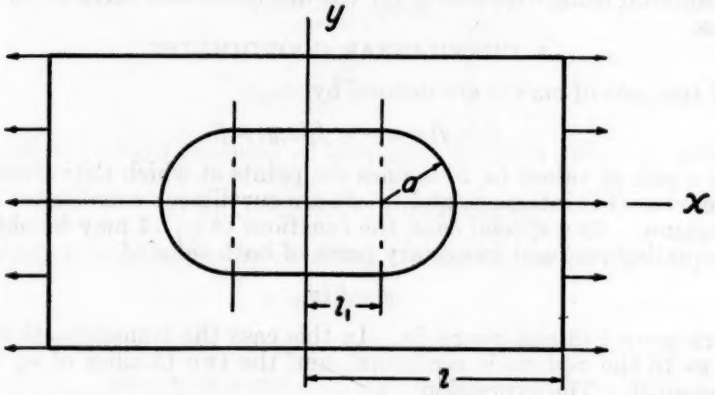


FIGURE 3.—*Ovaloid hole in plate subjected to uniform tension parallel to long axis of ovaloid.*

the long axis of the perforation in the direction of the load. As an approximation, u_p may be taken as its value in Kirsch's problem plus Pl_1/A_nE, that is,

$$u_p=\frac{Pl_1}{A_nE}+\frac{3P(x-l_1)}{C(n)A_gE}=\frac{P}{EA_g}\left[\frac{A_g}{A_n}l_1+\frac{3}{C(n)}(x-l_1)\right].$$

Substitution of this value of u_p in eq 2 gives

$$K=\frac{1}{1+\frac{1}{A_gl}\int\left[\frac{A_g}{A_n}l_1+\frac{3}{C(n)}(x-l_1)\right]tdy}.$$

As before, A_gl is one-half of V_g, the gross volume of one bay; $\int l_1tdy$ is one-half of V_r, the volume of the rectangular portion of the perforation; and $\int(x-l_1)tdy$ is one-half of V_c, the volume of the circular portion of the perforation. Hence

$$K=\frac{1}{1+\frac{A_g}{A_n}\frac{V_r}{V_g}+\frac{3}{C(n)}\frac{V_c}{V_g}}. \tag{13}$$

IV. ELLIPTICAL PERFORATIONS

1. GENERAL

The problem of a small elliptical hole in a plate subjected to uniform tension, S, in any direction at a large distance from the hole was solved by Inglis [5]. The method of Inglis amounts to assuming expressions for the displacements in the case of plane strain and determining constants to satisfy the state of stress at the boundary. The solution as given is not directly applicable to the determination of the displacements in the case of plane stress; hence it is proposed to repeat the solution using expressions for the displacements suitable for plane stress.

2. CURVILINEAR COORDINATES

If two sets of curves are defined by

$$f_1(x,y)=\alpha, \qquad f_2(x,y)=\beta, \tag{14}$$

then a pair of values (α, β) defines the points at which the corresponding curves (14) intersect, and (α, β) are curvilinear coordinates in the x, y-plane. As a special case, the functions of eq 14 may be obtained by equating real and imaginary parts of both sides of

$$w=F(z), \tag{15}$$

where $w=\alpha+i\beta$ and $z=x+iy$. In this case the transformation from the w- to the z-plane is conformal, and the two families of eq 14 are orthogonal. The expression

$$\frac{dz}{dw}=\frac{1}{h}e^{i\phi}, \tag{16}$$

defines the "stretch ratio," $1/h$, of the transformation, and gives ϕ, the inclination of the curve, β=constant, to the x-axis.

If u_α and u_β are the components of the displacement in the directions α-increasing, β-increasing, respectively, and

$$u=u_\alpha/h, \qquad v=u_\beta/h, \tag{17}$$

the components of strain are

$$\left.\begin{aligned}
\epsilon_\alpha&=h^2\frac{\partial u}{\partial\alpha}+\frac{u}{2}\frac{\partial h^2}{\partial\alpha}-\frac{v}{2}\frac{\partial h^2}{\partial\beta},\\
\epsilon_\beta&=h^2\frac{\partial v}{\partial\beta}+\frac{v}{2}\frac{\partial h^2}{\partial\beta}-\frac{u}{2}\frac{\partial h^2}{\partial\alpha},\\
\gamma_{\alpha\beta}&=h^2\left(\frac{\partial v}{\partial\alpha}+\frac{\partial u}{\partial\beta}\right)+u\frac{\partial h^2}{\partial\beta}+v\frac{\partial h^2}{\partial\alpha},
\end{aligned}\right\} \tag{18}$$

and the surface dilatation is

$$e=\epsilon_\alpha+\epsilon_\beta=h^2\left(\frac{\partial u}{\partial\alpha}+\frac{\partial v}{\partial\beta}\right). \tag{19}$$

The rotation is

$$\omega=\frac{h^2}{2}\left(\frac{\partial v}{\partial\alpha}-\frac{\partial u}{\partial\beta}\right). \tag{20}$$

For plane stress and in the absence of body forces, $e/(1-\nu)+i\omega$ is a function of z, and hence of w, or

$$\frac{e}{1-\nu}+i\omega=f(w). \tag{21}$$

The stresses are related to the strains by Hooke's law, which for plane stress is

$$\left.\begin{aligned}\sigma_\alpha&=\frac{E}{1-\nu^2}(\epsilon_\alpha+\nu\epsilon_\beta),\\ \sigma_\beta&=\frac{E}{1-\nu^2}(\epsilon_\beta+\nu\epsilon_\alpha),\\ \tau_{\alpha\beta}&=\frac{E}{2(1+\nu)}\gamma_{\alpha\beta},\end{aligned}\right\} \tag{22}$$

where E is Young's modulus of elasticity, and ν is Poisson's ratio.

3. ELLIPTICAL COORDINATES

Elliptical coordinates are obtained by writing for eq 15

$$z=c\cosh w, \tag{23}$$

from which

$$x=c\cosh\alpha\cos\beta, \qquad y=c\sinh\alpha\sin\beta. \tag{24}$$

Elimination of β from eq 24 gives

$$\frac{x^2}{c^2\cosh^2\alpha}+\frac{y^2}{c^2\sinh^2\alpha}=1, \tag{25}$$

a family of confocal ellipses with foci at $(\pm c, 0)$ and with semiaxes $c\cosh\alpha$ and $c\sinh\alpha$ (fig. 4). Elimination of α from eq 24 gives

$$\frac{x^2}{c^2\cos^2\beta}-\frac{y^2}{c^2\sin^2\beta}=1,$$

a family of hyperbolas confocal with and orthogonal to the ellipses of eq 25 (fig. 4).

For large α, the elliptical coordinates (α, β) approach the polar coordinates (r, θ) in the following manner:

$$\lim_{\alpha=\infty}\frac{c}{2}e^\alpha=r,$$

$$\lim_{\alpha=\infty}\beta=\theta.$$

Eq 16 becomes

$$\frac{dz}{dw}=\frac{1}{h}e^{i\phi}=c\sinh w$$

from which

$$h^2=\frac{2}{c^2(\cosh 2\alpha-\cos 2\beta)} \tag{26}$$

and

$$\tan \phi = \coth \alpha \tan \beta. \tag{27}$$

Also,

$$\frac{\partial h^2}{\partial \alpha} = -\frac{4}{c^2} \frac{\sinh 2\alpha}{(\cosh 2\alpha - \cos 2\beta)^2}, \tag{28}$$

$$\frac{\partial h^2}{\partial \beta} = -\frac{4}{c^2} \frac{\sin 2\beta}{(\cosh 2\alpha - \cos 2\beta)^2}. \tag{29}$$

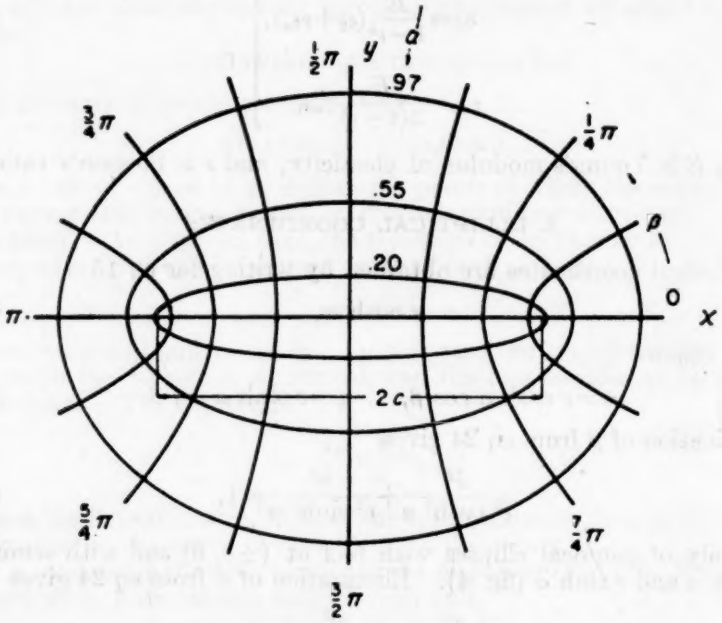


FIGURE 4.—*Elliptical coordinates.*

Denote by $\alpha = \alpha_0$ the ellipse

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1. \tag{30}$$

Then on the ellipse (eq 30), from eq 24 and 25,

$$\left.\begin{aligned} c \cosh \alpha_0 &= a, & c \sinh \alpha_0 &= b, \\ \cos \beta &= \frac{x}{a}, & \sin \beta &= \frac{y}{b}, \\ \cos 2\beta &= \frac{x^2}{a^2} - \frac{y^2}{b^2}, & \sin 2\beta &= \frac{2xy}{ab}, \\ \cosh 2\alpha_0 &= \frac{a^2+b^2}{c^2}, & e^{2\alpha_0} &= \frac{a+b}{a-b}, \end{aligned}\right\} \tag{31}$$

and from eq 27 and 31,

$$\cos\phi=h_0\frac{b}{a}x, \qquad \sin\phi=h_0\frac{a}{b}y, \tag{32}$$

where h_0 is the value of h on $\alpha=\alpha_0$.

4. INGLIS' PROBLEM FOR PLANE STRESS

The conditions of this problem may be satisfied by taking eq 21 as

$$\frac{e}{1-\nu}+i\omega=c_n\frac{e^{-nw}}{\sinh w}, \tag{33}$$

where n is any integer and c_n is a real constant for any n. Substitution in eq 33 of the expressions for e and ω given in eq 19 and 20 gives, upon equating real and imaginary parts,

$$\left.\begin{aligned}\frac{\partial u}{\partial\alpha}+\frac{\partial v}{\partial\beta}&=\frac{c^2(1-\nu)c_n}{2}[e^{-(n-1)\alpha}\cos(n+1)\beta-e^{-(n+1)\alpha}\cos(n-1)\beta],\\ \frac{\partial v}{\partial\alpha}-\frac{\partial u}{\partial\beta}&=c^2c_n[-e^{-(n-1)\alpha}\sin(n+1)\beta+e^{-(n+1)\alpha}\sin(n-1)\beta].\end{aligned}\right\} \tag{34}$$

The solution of eq 34 is

$$u=a_n[(n+p)e^{-(n-1)\alpha}\cos(n+1)\beta+(n-p)e^{-(n+1)\alpha}\cos(n-1)\beta]+\phi,$$
$$v=a_n[(n-p)e^{-(n-1)\alpha}\sin(n+1)\beta+(n+p)e^{-(n+1)\alpha}\sin(n-1)\beta]+\psi,$$

where

$$p=\frac{3-\nu}{1+\nu},$$

a_n is constant for any n, and $u=\phi$, $v=\psi$, is the solution of the homogeneous equation corresponding to eq 34. Suitable values of ϕ and ψ are

$$\phi=b_me^{-m\alpha}\cos m\beta, \qquad \psi=b_me^{-m\alpha}\sin m\beta,$$

where m is any integer and b_m is constant for any m. Hence

$$\left.\begin{aligned}u&=a_n[(n+p)e^{-(n-1)\alpha}\cos(n+1)\beta+(n-p)e^{-(n+1)\alpha}\cos(n-1)\beta]\\ &\quad+b_me^{-m\alpha}\cos m\beta,\\ v&=a_n[(n-p)e^{-(n-1)\alpha}\sin(n+1)\beta+(n+p)e^{-(n+1)\alpha}\sin(n-1)\beta]\\ &\quad+b_me^{-m\alpha}\sin m\beta.\end{aligned}\right\} \tag{35}$$

The strains may be calculated from eq 35 by means of eq 18. These are given by

$$\begin{aligned}c^2(\cosh 2\alpha-\cos 2\beta)^2\epsilon_\alpha=na_n\{&(n-2+p)e^{-(n-1)\alpha}\cos(n+3)\beta\\ &+(n+2-p)e^{-(n+1)\alpha}\cos(n-3)\beta\\ &-[(n+p)e^{-(n-3)\alpha}+2(p-1)e^{-(n+1)\alpha}]\cos(n+1)\beta\\ &-[(n-p)e^{-(n+3)\alpha}-2(p-1)e^{-(n-1)\alpha}]\cos(n-1)\beta\}\\ &-b_m\{[(m+1)e^{-(m-2)\alpha}+(m-1)e^{-(m+2)\alpha}]\cos m\beta\\ &-(m+1)e^{-m\alpha}\cos(m-2)\beta-(m-1)e^{-m\alpha}\cos(m+2)\beta\},\end{aligned}$$

$$c^2(\cosh 2\alpha-\cos 2\beta)^2\epsilon_\beta=na_n\{-(n-p)e^{-(n-1)\alpha}\cos(n+3)\beta$$
$$-(n+p)e^{-(n+1)\alpha}\cos(n-3)\beta$$
$$+[(n+2-p)e^{-(n-3)\alpha}-2(p-1)e^{-(n+1)\alpha}]\cos(n+1)\beta$$
$$+[(n-2+p)e^{-(n+3)\alpha}+2(p-1)e^{-(n-1)\alpha}]\cos(n-1)\beta\}$$
$$+b_m\{[(m+1)e^{-(m-2)\alpha}+(m-1)e^{-(m+2)\alpha}]\cos m\beta$$
$$-(m+1)e^{-m\alpha}\cos(m-2)\beta-(m-1)e^{-m\alpha}\cos(m+2)\beta\},$$

$$\frac{c^2}{2}(\cosh 2\alpha-\cos 2\beta)^2\gamma_{\alpha\beta}=na_n\{(n-1)e^{-(n-1)\alpha}\sin(n+3)\beta$$
$$+(n+1)e^{-(n+1)\alpha}\sin(n-3)\beta$$
$$-(n+1)e^{-(n-3)\alpha}\sin(n+1)\beta-(n-1)e^{-(n+3)\alpha}\sin(n-1)\beta\}$$
$$-b_m\{[(m+1)e^{-(m-2)\alpha}+(m-1)e^{-(m+2)\alpha}]\sin m\beta$$
$$-(m-1)e^{-m\alpha}\sin(m+2)\beta-(m+1)e^{-m\alpha}\sin(m-2)\beta\}.$$

Substitution of these expressions in eq 22 gives for the stresses

$$(\cosh 2\alpha-\cos 2\beta)^2\sigma_\alpha=A_n\{(n+1)e^{-(n-1)\alpha}\cos(n+3)\beta$$
$$+(n-1)e^{-(n+1)\alpha}\cos(n-3)\beta$$
$$-[(n+3)e^{-(n-3)\alpha}+4e^{-(n+1)\alpha}]\cos(n+1)\beta$$
$$-[(n-3)e^{-(n+3)\alpha}-4e^{-(n-1)\alpha}]\cos(n-1)\beta\}$$
$$+B_m\{-[(m+1)e^{-(m-2)\alpha}+(m-1)e^{-(m+2)\alpha}]\cos m\beta$$
$$+(m+1)e^{-m\alpha}\cos(m-2)\beta$$
$$+(m-1)e^{-m\alpha}\cos(m+2)\beta\}, \tag{36a}$$

$$(\cosh 2\alpha-\cos 2\beta)^2\sigma_\beta=A_n\{-(n-3)e^{-(n-1)\alpha}\cos(n+3)\beta$$
$$-(n+3)e^{-(n+1)\alpha}\cos(n-3)\beta$$
$$+[(n-1)e^{-(n-3)\alpha}-4e^{-(n+1)\alpha}]\cos(n+1)\beta$$
$$+[(n+1)e^{-(n+3)\alpha}+4e^{-(n-1)\alpha}]\cos(n-1)\beta\}$$
$$+B_m\{[(m+1)e^{-(m-2)\alpha}+(m-1)e^{-(m+2)\alpha}]\cos m\beta$$
$$-(m+1)e^{-m\alpha}\cos(m-2)\beta$$
$$-(m-1)e^{-m\alpha}\cos(m+2)\beta\}, \tag{36b}$$

$$(\cosh 2\alpha-\cos 2\beta)^2\tau_{\alpha\beta}=A_n\{(n-1)e^{-(n-1)\alpha}\sin(n+3)\beta$$
$$+(n+1)e^{-(n+1)\alpha}\sin(n-3)\beta$$
$$-(n+1)e^{-(n-3)\alpha}\sin(n+1)\beta$$
$$-(n-1)e^{-(n+3)\alpha}\sin(n-1)\beta\}$$
$$+B_m\{-[(m+1)e^{-(m-2)\alpha}+(m-1)e^{-(m+2)\alpha}]\sin m\beta$$
$$+(m+1)e^{-m\alpha}\sin(m-2)\beta$$
$$+(m-1)e^{-m\alpha}\sin(m+2)\beta\}, \tag{36c}$$

where

$$A_n=\frac{nE}{(1+\nu)c^2}a_n, \qquad B_m=\frac{E}{(1+\nu)c^2}b_m. \tag{37}$$

This solution can be adapted to the case of an elliptical hole (eq 30) in a large plate subjected, at a large distance from the hole, to the uniform stresses $\sigma_x=S_x$, $\sigma_y=S_y$, $\tau_{xy}=0$. The boundary conditions in elliptical coordinates are

$$\left.\begin{aligned}
&\sigma_\alpha=\tau_{\alpha\beta}=0, \ (\alpha=\alpha_0);\\
&\sigma_\alpha=\frac{S_x+S_y}{2}+\frac{S_x-S_y}{2}\cos 2\beta,\\
&\sigma_\beta=\frac{S_x+S_y}{2}-\frac{S_x-S_y}{2}\cos 2\beta,\\
&\tau_{\alpha\beta}=-\frac{S_x-S_y}{2}\sin 2\beta, \ (\alpha=\infty).
\end{aligned}\right\} \tag{38}$$

These conditions can be satisfied by summing the solutions (eq 36) for $n=1, -1; m=2, 0, -2$; with values for A_n, B_m,

$$\left.\begin{aligned} A_1&=\frac{e^{2\alpha_0}}{8}(S_x-S_y)-\frac{1}{16}(S_x+S_y), \qquad A_{-1}=-\frac{1}{16}(S_x+S_y),\\ B_0&=-\frac{1}{4}(S_x-S_y)+\frac{\cosh 2\alpha_0}{4}(S_x+S_y),\\ B_2&=-\frac{e^{4\alpha_0}}{8}(S_x-S_y), \qquad B_{-2}=\frac{1}{8}(S_x-S_y). \end{aligned}\right\} \tag{39}$$

The stresses are given by

$$\begin{aligned}(\cosh 2\alpha-\cos 2\beta)^2\sigma_\alpha=\frac{S_x-S_y}{8}\{&-[e^{2\alpha}-2e^{2\alpha_0}+e^{2(2\alpha_0-\alpha)}]\cos 4\beta\\ &+[e^{4\alpha}-4e^{2(\alpha_0+\alpha)}+3(e^{4\alpha_0}+1)-4e^{2(\alpha_0-\alpha)}+e^{4(\alpha_0-\alpha)}]\cos 2\beta\\ &-e^{2\alpha}+4e^{2\alpha_0}-(3e^{4\alpha_0}+2)e^{-2\alpha}+2e^{2(\alpha_0-2\alpha)}\}\\ &+\frac{S_x+S_y}{2}(\cosh 2\alpha-\cosh 2\alpha_0)\sinh 2\alpha, \end{aligned} \tag{40a}$$

$$\begin{aligned}(\cosh 2\alpha-\cos 2\beta)^2\sigma_\beta=\frac{S_x-S_y}{8}\{&[e^{2\alpha}+2e^{2\alpha_0}+e^{2(2\alpha_0-\alpha)}]\cos 4\beta\\ &-[e^{4\alpha}+3(e^{4\alpha_0}+1)+8e^{2(\alpha_0-\alpha)}+e^{4(\alpha_0-\alpha)}]\cos 2\beta\\ &+e^{2\alpha}+4e^{2\alpha_0}+(3e^{4\alpha_0}+2)e^{-2\alpha}+2e^{2(\alpha_0-2\alpha)}\}\\ &+\frac{S_x+S_y}{2}(\cosh 2a+\cosh 2\alpha_0-2\cos 2\beta)\sinh 2\alpha, \end{aligned} \tag{40b}$$

$$\begin{aligned}(\cosh 2\alpha-\cos 2\beta)^2\tau_{\alpha\beta}=\frac{S_x-S_y}{8}\{&[e^{2\alpha}-e^{2(2\alpha_0-\alpha)}]\sin 4\beta\\ &-[e^{4\alpha}+2e^{2(\alpha_0+\alpha)}-3e^{4\alpha_0}-1+2e^{2(\alpha_0-\alpha)}-e^{4(\alpha_0-\alpha)}]\sin 2\beta\}\\ &+\frac{S_x+S_y}{2}(\cosh 2\alpha-\cosh 2\alpha_0)\sin 2\beta. \end{aligned} \tag{40c}$$

From eq 37 and 39,

$$\left.\begin{aligned} a_1&=\frac{(1+\nu)c^2}{16E}[2e^{2\alpha_0}(S_x-S_y)-(S_x+S_y)], \qquad a_{-1}=\frac{(1+\nu)c^2}{16E}(S_x+S_y),\\ b_0&=\frac{(1+\nu)c^2}{16E}[4\cosh 2\alpha_0(S_x+S_y)-4(S_x-S_y)],\\ b_2&=-\frac{(1+\nu)c^2}{16E}2e^{4\alpha_0}(S_x-S_y), \qquad b_{-2}=\frac{(1+\nu)c^2}{16E}2(S_x-S_y). \end{aligned}\right\} \tag{41}$$

Substitution of the constants (eq 41) into eq 35 gives, in consideration of eq 17, for the displacements

$$\begin{aligned}\frac{8E}{c^2h}u_\alpha=(S_x-S_y)\{&4e^{2\alpha_0}\cos 2\beta-2(1-\nu)e^{2(\alpha_0-\alpha)}\\ &+(1+\nu)[(e^{2\alpha}-e^{2(2\alpha_0-\alpha)})\cos 2\beta-2]\}\\ &-2(S_x+S_y)[2\cos 2\beta-(1-\nu)\cosh 2\alpha-(1+\nu)\cosh 2\alpha_0], \end{aligned} \tag{42a}$$

$$\frac{8E}{c^2h}u_\beta=-(S_x-S_y)\{2(1-\nu)e^{2\alpha_0}+(1+\nu)[e^{2(2\alpha_0-\alpha)}+e^{2\alpha}]\}\sin 2\beta. \tag{42b}$$

On the boundary $\alpha=\alpha_0$ the displacements u_α and u_β of eq 42 assume the values

$$\left.\begin{aligned} u_\alpha&=\frac{h_0c^2}{2E}[(S_x-S_y)(e^{2\alpha_0}\cos 2\beta-1)+(S_x+S_y)(\cosh 2\alpha_0-\cos 2\beta)],\\ u_\beta&=-\frac{h_0c^2}{2E}(S_x-S_y)e^{2\alpha_0}\sin 2\beta. \end{aligned}\right\} \tag{43}$$

The components of the displacement along the x- and y-axes are obtained from eq 43 by the simple resolution

$$\left.\begin{aligned} u_x&=u_\alpha\cos\phi-u_\beta\sin\phi,\\ u_y&=u_\alpha\sin\phi+u_\beta\cos\phi. \end{aligned}\right\} \tag{44}$$

Substitution in eq 44 of the values of u_α and u_β from eq 43 and of $\sin\phi$ and $\cos\phi$ from eq 32 gives, after reduction effected by means of eq 31

$$u_x=\left[\frac{a+b}{a}(S_x-S_y)+\frac{b}{a}(S_x+S_y)\right]\frac{x}{E}, \tag{45}$$

$$u_y=-\left[\frac{a+b}{b}(S_x-S_y)-\frac{a}{b}(S_x+S_y)\right]\frac{y}{E}. \tag{46}$$

These are the rectangular components of the displacement on the bounding ellipse $\alpha=\alpha_0$, or $(x^2/a^2)+(y^2/b^2)=1$.

5. AXIAL RIGIDITY FOR LOAD PARALLEL TO MAJOR AXIS OF ELLIPSE

In this case the value to be substituted for u_p in eq 2 is the value of u_x from eq 45 with $S_y=0$, that is,

$$u_p=\left(1+2\frac{b}{a}\right)\frac{S_xx}{E}. \tag{47}$$

It has been shown [5] that the correction factor to be applied to the load P of eq 2 is approximately independent of the shape of the elliptical hole. Hence, for most practical cases, P is given by eq 11 (derived for a circular hole), i. e.,

$$P=S_xA_g\left(1-\frac{1}{2n^2}-\frac{1}{2n^4}\right)=S_xA_gC(n),$$

where

$$n=\frac{A_g}{2bt}=\frac{A_g}{A_g-A_n}.$$

[5] See p. 545 of reference [4].

Equation 2 becomes

$$K=\frac{1}{1+\frac{1+2\frac{b}{a}}{C(n)}\int xtdy}=\frac{1}{1+\frac{1+2\frac{b}{a}}{C(n)}\frac{V_0}{V_g}}, \tag{48}$$

where V_0 is the volume of the perforation and V_g is the gross volume of one bay of the tension member.

6. AXIAL RIGIDITY FOR LOAD PARALLEL TO MINOR AXIS OF ELLIPSE

In this case the load is in the direction of the y-axis, and dy in eq 2 should be replaced by dx. The value of u_p is that of u_y from eq 46 with $S_x=0$, i. e.,

$$u_p=\left(1+2\frac{a}{b}\right)\frac{S_y y}{E}.$$

Again,

$$P=S_p A_g\left(1-\frac{1}{2n^2}-\frac{1}{2n^4}\right)=S_y A_g C(n),$$

where

$$n=\frac{A_g}{2at}=\frac{A_g}{A_g-A_n},$$

and eq 2 becomes, finally,

$$K=\frac{1}{1+\frac{1+2\frac{a}{b}}{C(n)}\frac{V_0}{V_g}}. \tag{49}$$

V. TESTS ON TENSION MEMBERS HAVING CIRCULAR PERFORATIONS

1. GENERAL

The approximations employed in the derivation of eq 12, 13, 48, and 49 may be expected to introduce appreciable error if the perforations are too wide or if the spacing of the perforations is too small. Hence it was considered desirable to make some tests which would indicate the limits of the ranges of variables over which the formulas give satisfactory results.

Time for an extensive experimental investigation was not available; the work therefore was confined to the verification of eq 12 for circular holes.

For the case of a thin rectangular strip of width w and thickness t, with a series of circular holes of diameter d at midwidth and spaced uniformly l on centers, eq 12 becomes

$$\frac{1}{K}=1+\frac{3\pi}{4\left(n-\frac{1}{2n}-\frac{1}{2n^3}\right)\frac{l}{d}},\left(\frac{l}{d}\geqslant 1\right), \tag{50}$$

where $n=w/d$.

It is easy to see that eq 50 will fail for sufficiently low l/d. The perforated strip cannot have an axial rigidity as low as that of an

unperforated strip of width $w-d$, that is, K must be greater than $(n-1)/n$. Yet eq 50 gives K less than $(n-1)/n$ for

$$1<\frac{l}{d}<\frac{2.3562}{1+\frac{1}{n}+\frac{1}{2n^2}+\frac{1}{2n^3}}. \tag{51}$$

The lower limit of l/d (as a function of n) for which eq 50 is satisfactory is perhaps best determined by experiment. The same is true of n, since it is to be expected, from the method of derivation of eq 12, that eq 50 will fail for sufficiently low n.

2. DESCRIPTION

Tests were made on strips, 26 in. long, ¾ in. wide, and 0.079 in. thick, of aluminum alloy 24ST. There were four strips, one corresponding to each of the following values of n: 5.84, 3.87, 2.92, 1.94.

The axial rigidity of each strip was measured before any holes had been made in it. Holes were then subdrilled in each strip and reamed to give the proper value of n. The holes were at midwidth of the strip and uniformly spaced along the length so that there were an integral number of bays in a 10-in. gage length. The axial rigidity of the perforated strip was measured, and then additional holes were made to halve the value of l/d, and so on successively until five tests had been made on each strip. The values of l/d follow.

$n=5.84$, $l/d=\infty$, 11.11, 5.56, 2.78, 1.39

$n=3.87$, $l/d=\infty$, 12.92, 6.46, 3.23, 1.61

$n=2.92$, $l/d=\infty$, 12.97, 6.49, 3.24, 1.62

$n=1.94$, $l/d=\infty$, 12.95, 6.48, 3.24, 1.62

The stretch in a 10-in. gage length due to increasing the load from about 50 lb. to about 550 lb was measured for each value of l/d. For a given n, the stretch for the unperforated strip ($l/d=\infty$) divided by the stretch for a perforated strip gives the value of K for the perforated strip.

The strips were held in Templin grips and loaded by dead weights (the same initial and final weights were used throughout) raised and lowered with the jack of an Amsler vertical hydraulic testing machine. The stretch was measured using a pair of 10-in. gage-length Tuckerman optical strain gages provided with either 0.2-in. or 0.5-in. lozenges.

The permanent set produced by the 550-lb load was negligible in each case.

The test setup is shown in figure 5.

3. RESULTS

The results of the tests and a comparison of the observed with the theoretical values of K are shown in figure 6.

For l/d greater than about 3, the error in the theoretical K increases with decreasing n and is about 0.02 to 0.03 for n about 2.

For small l/d, the theoretical K is too low, especially for large n.

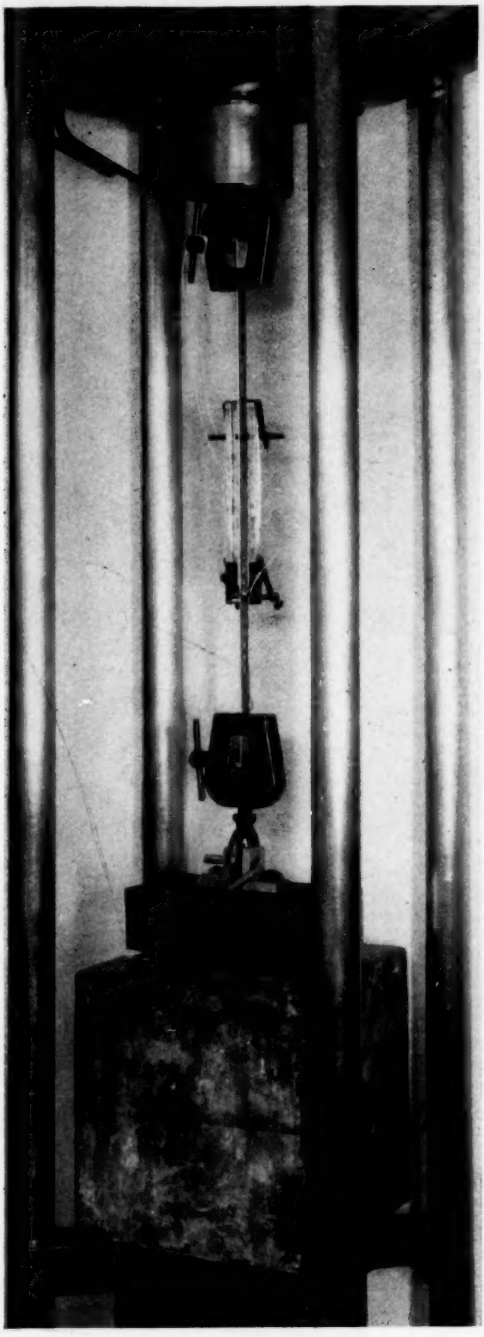


FIGURE 5.—*General view of test setup.*

These results indicate that eq 50 can be relied upon to give K within 0.03 for $n>2$, $l/d>2$, and within perhaps 0.015 for $n>3$, $l/d>3$

VI. SUMMARY

Approximate formulas have been developed for the computation of the axial rigidity of a long tension or compression member containing a plate of constant thickness uniformly perforated with a series of circular, elliptical, or ovaloid holes.

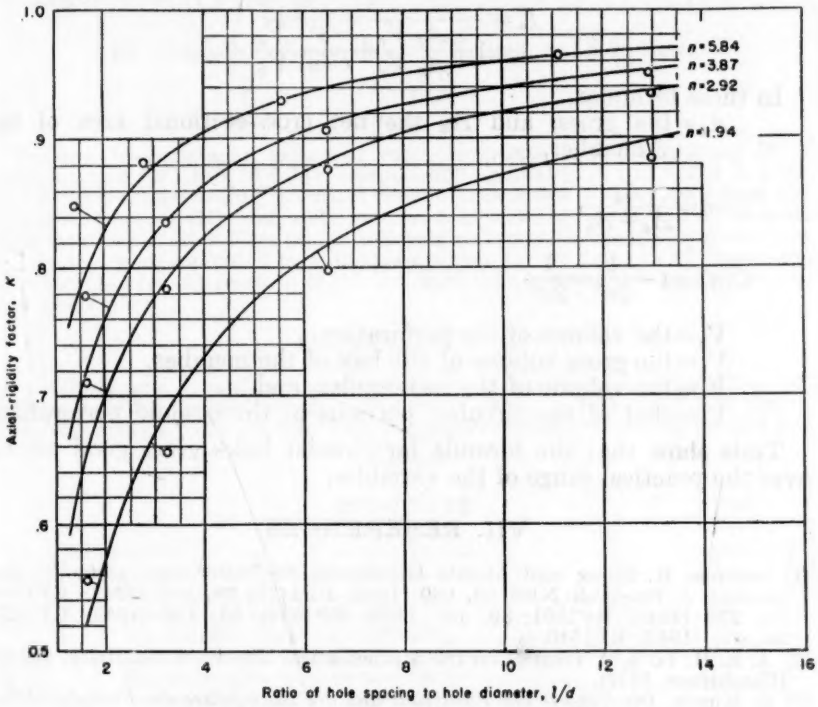


FIGURE 6.—*Variation of K with n and l/d*

The curves show the theoretical values (eq 50), the circles the observed values.

The axial-rigidity factor K is defined so that KEA_g is the rigidity which should be used in place of EA_g in the ordinary formula for computation of the extension of the member.

The formulas for K are:

for circular holes,

$$K=\frac{1}{1+\frac{3}{C(n)}\frac{V_0}{V_g}};$$

for elliptical holes of semimajor axis a and semiminor axis b,

$$K=\frac{1}{1+\frac{1+2\frac{b}{a}}{C(n)}\frac{V_0}{V_g}},$$

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if the load is parallel to the major axis, and

$$K=\frac{1}{1+\dfrac{1+2\dfrac{a}{b}}{C(n)}\dfrac{V_0}{V_g}},$$

if the load is parallel to the minor axis of the ellipse; and for ovaloid holes

$$K=\frac{1}{1+\dfrac{A_g}{A_n}\dfrac{V_r}{V_g}+\dfrac{3}{C(n)}\dfrac{V_c}{V_g}}.$$

In these formulas,

A_g=the gross, and A_n the net cross-sectional area of the member,

$$n=\frac{A_g}{A_g-A_n},$$

$$C(n)=1-\frac{1}{2n^2}-\frac{1}{2n^4},$$

V_0=the volume of the perforation,
V_g=the gross volume of one bay of the member,
V_r=the volume of the rectangular, and
V_c=that of the circular, portions of the ovaloid perforation.

Tests show that the formula for circular holes gives good results over the practical range of the variables.

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INGTON, September 22, 1943.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1569

Part of Journal of Research of the National Bureau of Standards, Volume 31, December 1943

BASIC IONIZATION CONSTANT OF METACRESOLSULFONPHTHALEIN; pH VALUES AND SALT EFFECTS

By Elizabeth E. Sager, Harry J. Keegan, and S. F. Acree

ABSTRACT

Spectral transmittancy values at room temperatures approximating 25° C were obtained for 1.25×10^{-5} *M* metacresolsulfonphthalein in water and in 0.001- to 8-*M* hydrochloric acid. In water the indicator exists in the yellow form (Y), and hydrogen ions (H) from acids convert it into the red form (R). The molar concentrations of each form of the indicator in various concentrations of hydrochloric acid were computed from the spectrophotometric data. The dissociation constant (K_b) for the reaction of the indicator with hydrochloric acid is given by the equation

$$K_b = M_H f_H M_Y f_Y / M_R f_R,$$

in which *M* and *f*, with appropriate subscripts, represent the molarities and activity coefficients, respectively. The value of K_b is 1.98×10^{-2} and that of $-\log K_b$ or pK_2 is 1.703 ± 0.005. The indicator is useful over the pH range 0 to 3.

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I. INTRODUCTION

Metacresolsulfonphthalein, commonly known as metacresolpurple, is a useful indicator for colorimetric pH determinations. It undergoes color changes from yellow (Y) to red (R) in acid solution and from yellow to purple (P) in alkaline solution, as indicated by the struc-

tural formulas in figure 1. The indicator is stable in both of its pH ranges. The application of spectrophotometric methods for the precise determination of pH values with an indicator [1] requires a knowledge of the absorptive properties of its different chemical forms, the nature of the transformation from one form to another, the states of equilibrium between the different chemical forms, the thermodynamic ionization constants, and the effects of electrolytes on the equilibrium and ionization constants and spectral properties. In this paper these properties are reported for the acid range of metacresolpurple; work is in progress on the alkaline range.

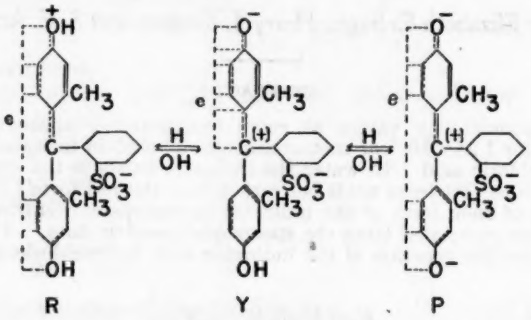

FIGURE 1.—*Metacresolsulfonphthalein in acid, neutral, and alkaline solutions.*

The dotted lines indicate resonance in the respective chromophores. The various colored forms, R, Y, and P, are, for convenience, considered in terms of the two most probable extreme resonant structures, one a pure quinone form and the other a dipolar benzenoid structure with a relatively large negative charge [−] on the oxygen of the quinone group and a corresponding positive charge [+] on the central carbon atom. The symbols representing these various forms are:

R⟷ =dipolar resonant red form.
Y⁻ =yellow form with typical quinone resonance and without [+] [−] charges.
Y⁻ ⟷ =dipolar resonant yellow form with [+] [−] charges.
P− − =purple form with quinone phenolate resonance and without [+] [−] charges.
P− − ⟷=dipolar resonant purple form with [+] [−] charges.

II. MATERIALS, EQUIPMENT, AND METHOD

1. MATERIALS

Metacresolsulfonphthalein, especially purified for this investigation, was obtained from W. A. Taylor & Co., Baltimore, Md. Before being weighed, the crystals were dried in an oven at 105° to 110° C for 2 hours. Hydrocholric acid that conformed to specifications of the American Chemical Society was used for making 2-*M* solutions from which the lower concentrations were prepared by volumetric procedures. The acidity was determined by titration with standard sodium hydroxide with phenolphthalein as indicator. Potassium chloride, barium chloride, and strontium chloride were each recrystallized twice and dried in an oven for several hours at 110° to 120° C.

2. PREPARATION OF THE SOLUTIONS

All the solutions were prepared by volumetric methods and are expressed as molar concentrations. A stock solution of metacresolsulfonphthalein, 2.5×10^{-4} *M* was made by dissolving 0.0956 g of the dried crystals in conductivity water and diluting to 1 liter. A day or more was required for the crystals to dissolve. From this

[1] See references [1 to 10] for literature on the theories of indicators, salt effects, and mass-law relations applicable in colorimtetric pH measurements.

stock solution, 5 or 10 ml, as desired, was transferred by pipet to each of the 100-ml volumetric flasks in which the mixtures to be studied were prepared. These amounts resulted in indicator solutions 1.25×10^{-5} *M* or 2.5×10^{-5} *M*, which concentrations were found convenient for the spectrophotometric measurements in the 1-cm absorption cells.

The stock solutions of hydrochloric acid and of salts were first filtered through a sintered-glass filtering crucible to remove any trace of dust or lint that might affect the absorption measurements. The required amounts of the acid solutions or of the salt solutions were added to the 100-ml volumetric flasks either by pipet or buret and diluted to the mark with conductivity water.

Two solutions were necessary for each spectrophotometric curve. The first contained the indicator in the desired medium—either water, acid, or acid and salt—and the other contained the same components of the solution without the indicator. For the amount of stock indicator used in the first solution, an equal volume of water was substituted in the solution without the indicator. All the solutions were freshly prepared, usually the day before the spectrophotometric determinations were made, but the indicator was added on the morning the measurements were made. Special tests showed that the indicator solutions were stable for several days.

3. SPECTROPHOTOMETRIC EQUIPMENT

The spectrophotometric measurements for the visible portion of the spectrum were made in the Photometry and Colorimetry Section of this Bureau, with a recording spectrophotometer of the Hardy type. The calibration and operation of this instrument have been described by Gibson and Keegan [11][2]. All the measurements were made with slits giving a spectral band approximately 4 mμ wide. Absorption cells for the solutions consisted of Pyrex cylindrical tubes with polished parallel ends fitted with removable round plates of polished quartz or Pyrex glass. A pair of blackened brass holders were fitted with sleeves to hold either 1-, 2-, or 5-cm absorption cells. In these experiments the beam of light passed through a layer of solution of 1 ± 0.001 cm. All the spectrophotometric measurements were made at room temperatures, varying from 23° to 28° C. The measurements for the ultraviolet portion of the spectrum were made by Geraldine W. Haupt, of the Photometry and Colorimetry Section of this Bureau, with a Hilger sectorphotometer and a Fuess quartz spectrograph, and by P. A. Cole and M. Eicher, of the National Institute of Health, Bethesda, Md., with a Spekker spectrophotometer.

4. SPECTROPHOTOMETRIC MEASUREMENTS IN THE VISIBLE SPECTRUM

The transmittancy data recorded for a typical series of spectrophotometric measurements are shown in figure 2. Each graph sheet is calibrated for wavelength by recording the transmission curve of a standardized didymium glass (Jena BG 11), the wavelengths of the transmission minima being accurately known. The wavelength cor-

[2] Figures in brackets indicate the literature references at the end of this paper.

rections are made as described by Gibson and Keegan. The curves at the 100-percent transmission line are obtained with identical absorption cells filled with water, or with acid-salt mixtures without indicator, and placed one in each of the two light beams of the instrument. The zero transmission curves are obtained by blocking out the light beam normally passing through the indicator solution. Such

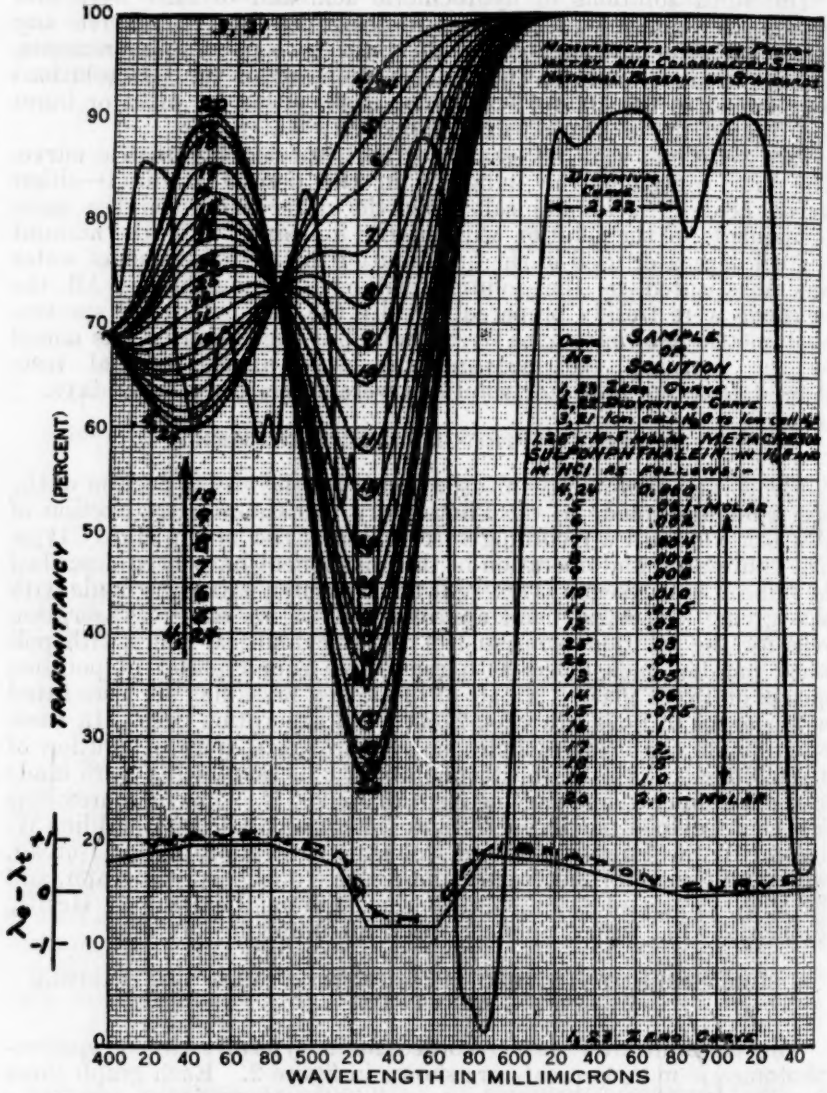

FIGURE 2.—*Recorded spectrophotometric curves showing the transformation of metacresolsulfonphthalein from yellow to red in hydrochloric acid.*

calibration curves are usually made at the beginning and end of each series of curves on one graph sheet. For each spectrophotometric curve of the indicator, one absorption cell is filled with the indicator solution and the other cell with its respective comparison solution.

In this manner the absorption of light by the solvent system and the reflections at the end plates of the cells are compensated, and only the percentage transmittancy of light by the indicator itself in the particular solvent system is recorded. The result is the transmittancy curve of the indicator over the spectral range 400 to 750 mμ.

The transmittancy curves shown in figure 2 represent the transformation [4, 5, 9] of metacresolsulfonphthalein from the yellow to the red form by increased amounts of hydrochloric acid from 0.001 to 2 *M*. The data in this figure were obtained with an indicator concentration of 1.25×10^{-5} *M*, and a cell depth of 1 cm. Additional spectrophotometric determinations were made with indicator concentrations of 0.625×10^{-5} and 2.5×10^{-5} *M* in the same cells to check the validity of Beer's law.

The transmittancy values, in percent, were read from the curves at wavelength intervals of 2, 4, or 10 mμ and were reduced to corresponding molar absorption indices, k, by the relation:

$$k=\frac{-\log_{10}t}{d\times M}, \tag{1}$$

in which t is transmittancy, d is the cell depth, in centimeters, and M is the molar concentration.

5. ELECTROMOTIVE FORCE MEASUREMENTS

Readings of pH at 25° C were made for each indicator solution and its comparison solution without the indicator, using a hydrogen-electrode assembly with saturated potassium chloride calomel half-cell and liquid junction. The hydrogen-electrode assembly was calibrated with 0.05 *m* potassium acid phthalate, pH 4.008, as described in the Bureau certificate for Standard Sample 84a issued by the National Bureau of Standards. The glass-electrode assembly for the pH meter was also calibrated with this buffer. Potentiometric readings were made first with the hydrogen-electrode assembly, then with the glass electrode. Corrections for the error caused by the liquid-junction potential were not applied. Measurements on some of the most concentrated salt solutions were not made because the salt solutions diffused through the saturated potassium chloride and equilibrium for the potentiometric measurement could not be reached. Since this work was done, it has been shown that these difficulties can be avoided and very precise pH data obtained by use of hydrogen and silver-silver–chloride electrodes in cells without liquid junctions to hold the solutions of indicators and buffers [13].

III. EXPERIMENTAL DATA

1. SPECTRAL ABSORPTIVE PROPERTIES OF METACRESOLSULFONPHTHALEIN IN THE VISIBLE AND ULTRAVIOLET

The molar absorption index curves for the visible and ultraviolet regions of the spectrum are given in figure 3 for the three colored forms of metacresolsulfonphthalein that are in neutral, acid, and alkaline solutions, respectively. The indices are plotted as a function of reciprocal wavelength, or wave number, and corresponding wavelengths are shown at the top of the figure. For measurements in the

visible region, 1.25×10^{-5} *M* solutions of metacresolsulfonphthalein were made in water, in 2-*M* hydrochloric acid, and in 1.25×10^{-3} *M* sodium hydroxide. The strong bands in the visible spectrum show maximum absorption for the neutral yellow form in water, curve Y, at a wave number of 22,940 cm^{-1} (wavelength 436 mμ); for the acid

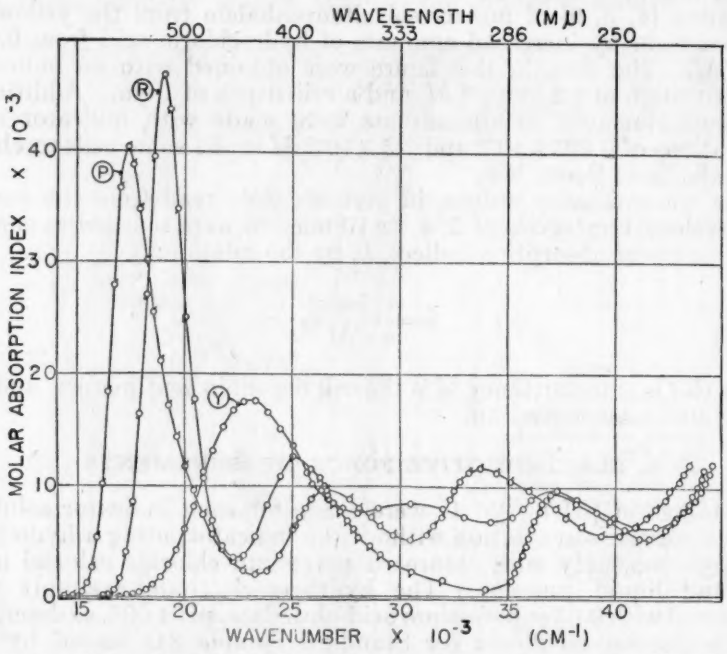

FIGURE 3.—*Molar absorption indices of the three forms of metacresolsulfonphthalein in the visible and ultraviolet portions of the spectrum.*

R, red form; Y, yellow form; P, purple form.

red form, curve R, at a wave number of 18,960 cm^{-1} (wavelength 527.5 mμ); and for the alkaline purple form, curve P, at a wave number of 17,360 cm^{-1} (wavelength 576 mμ).

For the ultraviolet [3] measurements, 1.25×10^{-4} *M* solutions of the indicator were used in water, in 2-*M* hydrochloric acid, and 1.25×10^{-2} *M* sodium hydroxide. The spectrophotometric data given in this paper are concerned mainly with the progressive shift of curves Y to R in the visible spectrum for acid solutions.

2. TRANSFORMATION OF METACRESOLSULFONPHTHALEIN FROM THE YELLOW TO THE RED FORM BY HYDROCHLORIC ACID

The transformation of metacresolsulfonphthalein from the yellow to the red form is shown by the 19 curves in figure 4 and appears to be approximately complete in 2-*M* hydrochloric acid. The effect of 1.5-, 2-, 4-, and 8-*M* acid has been studied separately and is shown

[3] The sulfonphthaleins and many other indicators contain, in addition to the chromophore, other groups (auxochromes) such as carboxylate and sulfonate radicals, which do not absorb visible light, and thus do not affect the calculations presented in this article. Recent measurements on sulfonates, benzoates, and other compounds of polar character show strong bands in the ultraviolet. Any computations on the Y, R, and P bands (fig. 3) to correlate the absorption indices of the chromophore for both the ultraviolet and visible regions must involve recognition of the resonance of the $-SO_3^-$ group and corrections for its own absorption indices in the ultraviolet.

by the additional absorption curves in figure 5. As the quantitative relations between the acidity of the solutions and the optical properties of the indicator, as expressed by the curves in figures 4 and 5, are the basis of the determination of pH values and salt effects with metacresolsulfonphthalein, these spectrophotometric curves will be considered in detail. Below 0.1-*M* acid, the increase in absorption index at any wave number with rise in hydrogen-ion activity is close to the values calculated by use of the mass-law equations discussed below. Between 0.1- and 2-*M* hydrochloric acid, the percentage change in index is slightly larger for the lower wave numbers of the absorption band for the red form (from the peak toward the red) than for the higher wave numbers of the band. The acid in concentrations from 0.5 to above 2 *M* begins noticeably to cause two compensating effects. The first is the completion of the normal reaction of hydrogen ions with the yellow form, which should slightly increase the index at wave

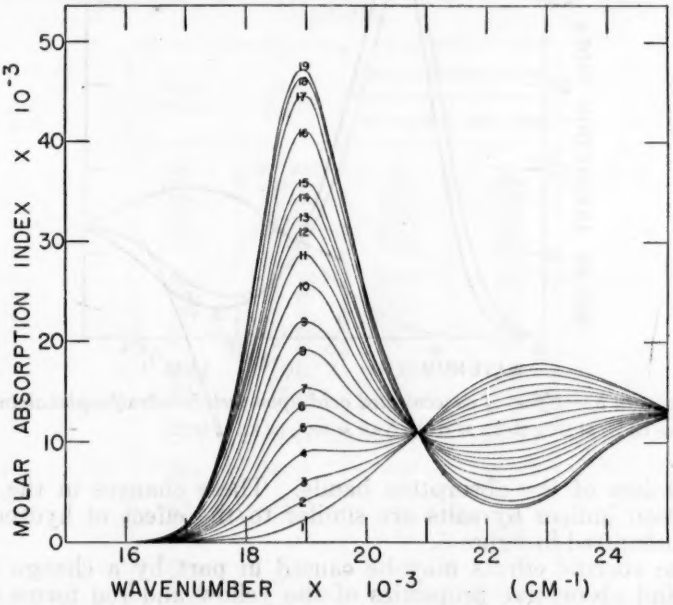

FIGURE 4.—*Transformation of metacresolsulfonphthalein from the yellow to the red form in hydrochloric acid.*

(1) No acid (yellow form); (2) 0.001 *M*; (3) 0.002 *M*; (4) 0.004 *M*; (5) 0.006 *M*; (6) 0.008 *M*; (7) 0.010 *M*; (8) 0.015 *M*; (9) 0.020 *M*; (10) 0.030 *M*; (11) 0.040 *M*; (12) 0.050 *M*; (13) 0.060 *M*; (14) 0.075 *M*; (15) 0.100 *M*; (16) 0.200 *M*; (17) 0.500 *M*; (18) 1.000 *M*; (19) 2.000 *M*.

number 18,960 (527.$_5$ mμ), and the second is the "abnormal" or specific, effect [1, 8, 21, 22] of the increased electrolyte and surrounding electrical field in decreasing the absorptive properties and index of the indicator, together with the shift of the absorption bands for the red and yellow forms toward the lower wave numbers. The net result is that the acid in concentrations above 2 *M* causes little additional change in the position and height of the main absorption band, except a slight shift, until a concentration of over 4 *M* is reached. With higher acid concentrations, as shown in curve 5, figure 5, there is a decrease in the index at the maximum and an increase at the mini-

mum, accompanied by a definite displacement of the isosbestic point.[4]

In order to determine whether these specific effects are due to acids alone or is a general property of all concentrated solutions of electrolytes, the effect of increasing amounts of salts on the absorptive properties of both the yellow and the red forms of the indicator is under investigation and details will be reported later. Neutral salts of low concentration have no important effect upon the absorptive properties of either form other than normal changes in transmittancy arising from variations in ionic strengths, activity coefficients, and ionization. Salts 2 *M* or higher in concentration, however, cause a slight shift in the isosbestic point and in the positions of the maxima

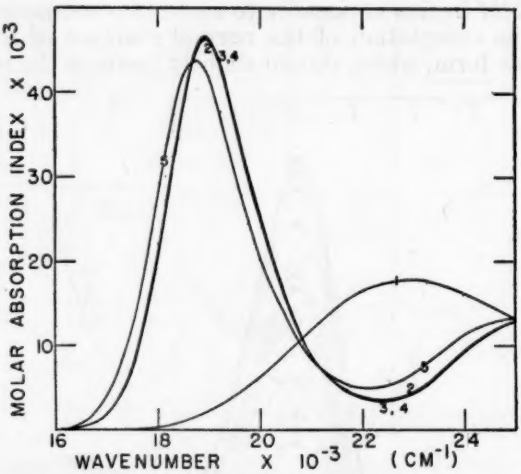

FIGURE 5.—*Effect of concentrated acid upon metacresolsulfonphthalein.*

(1) Water; (2) 1.5 *M* HCl; (3) 2.0 *M* HCl; (4) 4.0 *M* HCl; (5) 8.0 *M* HCl.

and minima of the absorption bands. These changes in the molar absorption indices by salts are similar to the effect of hydrochloric acid, illustrated in figure 5.

These specific effects may be caused in part by a change in the polar and absorptive properties of the yellow and red forms of the indicator in the altered electrical field, or it may denote the beginning of a new type of ionization, hydration, or intramolecular transformation into a lactone. In considering the sources of a new type of ion, a colored impurity is first suspected. In this case it is most likely to be a colored isomer with one or both phenols attached in the orthoposition instead of in the paraposition characteristic of the sulfonphthaleins (fig. 1). Small quantities of such orthoisomers might have absorption bands and low pH ranges which could account for the observed shifts. This explanation does not seem valid in view of the lack of such abnormalities in the spectrophotometric

[4] An isosbestic point is found at that wavelength or wave number at which the transmittancies or indices of the yellow and red forms are equal. The word "isobestic," which has appeared in various publications, should be spelled "isosbestic." The word originates from the Greek prefix ἴσος (isos, meaning equal) and the Greek root σβεστός (sbestos, meaning quenched or put out). The word "asbestos" is derived from the same root. Thus, "isosbestic point" means the point of equal extinction by the two colored forms of the indicator. The authors in a previous publication used the term "isobestic."

curves obtained recently in another study on metacresolsulfonphthalein in its high pH range, and particularly when a 500 to 1-*M* ratio of alkali to indicator is used to neutralize any orthoisomer present and probably having a pK value somewhat higher than that for metacresolsulfonphthalein. Formation of a colorless carbinol or lactone or of a dioxonium salt of the indicator would probably reduce the absorption index without a shift. The discussion below seems to eliminate the possibility that repression of the ionization of the sulfonate group accounts for these phenomena. As metacresolsulfonphthalein at pH 7.2 to 9 also shows such shifts of the absorption bands in concentrated salt solutions, we can conclude that the specific salt effect of the concentrated hydrochloric acid is due to the alteration of the spectral properties of the indicator chiefly by the change in the surrounding electrical field of the solutions [8].

TABLE 1.—*Molar absorption indices for the yellow and red forms of metacresolsulfonphthalein*

Wavelength [a]	Wave number	Molar absorption indices	
		Yellow form	Red form
$m\mu$	$cm^{-1} \times 10^{-3}$	k_Y	k_R
399.4	25.04	13390	12580
409.3	24.43	15110	11190
419.3	23.85	16550	8660
429.2	23.30	17570	5660
*436.3	22.93	17940	4270
439.1	22.77	17880	3920
449.1	22.27	17080	3570
459.1	21.78	15660	4470
469.1	21.32	13670	6650
*479.5	20.86	10930	10930
489.3	20.44	8700	16860
499.4	20.02	6490	24330
509.5	19.63	4600	34540
520.1	19.23	3010	44230
*527.5	18.96	2190	47080
530.7	18.84	1890	46870
540.7	18.49	1130	39810
550.7	18.16	630	27210
560.7	17.83	380	15780
570.3	17.54	210	8320
579.6	17.25	140	3740
589.3	16.97	70	1440
599.4	16.68	30	600
609.4	16.41	00	140
619.5	16.14	00	000

[a] The transmittancy values were read at even wavelength intervals from the graph sheet and then corrected to their true wavelengths. In addition, the values for the isobestic point and the maximum absorbancy for the red and yellow forms are given.

The specific salt effects are small and are neglected in the present practical applications of the spectrophotometric data for metacresolsulfonphthalein in hydrochloric acid solutions. Since the absorption index curve is nearly constant for acid contents between 2 and 4 *M*, the 2-*M* curve is taken here as the practical limit for the transformation of the yellow to the red form.[5] The molar absorption indices for various wavelengths and corresponding wave numbers representing the characteristic absorptive properties of the yellow and red forms of this indicator are given in table 1.

[5] A more precise evaluation of the magnitude of the index for partial and complete transformation and the quantitative formulation of the specific salt effects are under way.

3. COMPUTATION OF THE PERCENTAGES OF THE RED AND YELLOW FORMS OF THE INDICATOR FROM THE MOLAR ABSORPTION INDICES

If it be assumed that the corresponding curves for the partial transformation of the indicator (see figs. 2 and 4) represent linear combinations at each wavelength or wave number of different proportions of only two limiting absorption indices (curves 1 and 19, fig. 4), then the fraction (α) of the indicator changed from yellow to red at a given acid concentration is given by

$$k_\alpha = \alpha k_R + (1-\alpha)k_Y \text{ or } \alpha = (k_\alpha - k_Y)/(k_R - k_Y), \quad (2)$$

where k_Y, k_R, and k_α are, respectively, the molar absorption indices at a given wave number for the yellow, red, and mixed forms of the indicator [1, 4, 5, 6]. The values of k_Y, k_R, and k_α for all the wavelengths and concentrations of indicator, hydrochloric acid, and salts studied were computed from records like figure 2.

Calculations of α for different wavelengths near the maxima of the absorption bands are given in table 2. If the linear variation of k_α with respect to α expressed by eq 2 is strictly correct at all wavelengths, the α values for each curve should all be the same, regardless of wavelength. In general, however, there is a decrease in α with increase in wavelength in each of the bands (420 to 460 mμ and 518 to 540 mμ). The variation from constancy appears to be slightly greater than the estimated accidental variation arising from the experimental uncertainties in the recording and reading of the original transmittancy curves. Since this consistent variation of α occurs in the regions of the spectrum where the specific effects of high acid concentrations clearly affect the calculated values of α (see figs. 4 and 5), it may be ascribed to the same cause. The variation of α with respect to wavelength may be neglected in this paper. The average values of α are close to those found at 527.$_5$ mμ. Since the experimental absorption indices are most accurately determined at wavelength 527.$_5$ mμ (wave number 18,960) at the maximum of the absorption band for the red form, these indices alone, and the corresponding values of α, are given in table 3 and used in the calculations to be described.

From the approximate constancy of α across the spectrum, it is assumed that as the indicator is changed from yellow to red the characteristic absorption bands of the two chemical forms of the indicator are not appreciably shifted, broadened, or otherwise distorted as a result of changing the chemical and physical nature of the solvent medium, or as a result of the presence of more than two chemical forms or of association of the indicator.[6] These assumptions are further borne out by the existence of a sharply defined isosbestic point at wave number 20,860 (wavelength 479.$_5$ mμ) and molar absorption index 10,930. Since the absorption bands overlap, it follows that at least one wave number will be found at which the molar absorption indices of the yellow and red forms of the pure indicator, k_Y and k_R, will be equal for all values of α. Hence, as expressed linearly in eq 2, if a mixture of these two forms alone determines the observed absorp-

[6] If polar states (electronic tautomers or electromers) of each ion, indicated by [+] and [−] signs in figure 1, are present in instantaneous equilibrium with the nonpolar forms, the absorption bands may still be used at any given temperature to calculate the over-all values of α and $(1-\alpha)$ for the red and yellow ions, including their natural polar states or those "induced" by other ions [1, 4, 7, 8]. This point needs further study for development of exact equations.

tion curve in their overlapping regions of spectral absorption, the isosbestic point must remain unchanged with respect to both index and wave number for all stages of the color transformation. This may not be true when specific salt effects, association, or colored impurities affect this part of the spectrum, as shown in figure 5.

TABLE 2.—*Variations in the values of* α *as derived from the series of absorption indices at different acid concentrations and given wavelengths*

Wavelength	Molar concentration of hydrochloric acid										
$m\mu$	0.002	0.006	0.01	0.02	0.03	0.04	0.05	0.075	0.20	0.50	1.00
420	0.084	0.195	0.290	0.442	0.550	0.613	0.644	0.723	0.878	0.966	0.989
424	.087	.205	.287	.443	.545	.605	.649	.722	.882	.955	.995
428	.076	.200	.285	.443	.534	.606	.640	.717	.875	952	.989
432	.081	.206	.292	.442	.538	.605	.645	.720	.875	.958	.990
436	.082	.202	.292	.442	.534	.597	.644	.723	.868	.956	.988
440	.082	.203	.294	.439	.533	.596	.641	.720	.865	.952	.983
444	.081	.198	.288	.437	.530	.593	.638	.715	.865	.950	.983
448	.077	.200	.286	.438	.527	.590	.639	.712	.864	.946	.982
452	.083	.202	.288	.438	.531	.590	.638	.713	.864	.946	.982
456	.073	.194	.288	.432	.523	.586	.631	.711	.858	.940	.975
460	.082	.203	.288	.440	.532	.589	.633	.712	.863	.943	.975
518	.085	.207	.295	.444	.532	.598	.647	.730	.871	.947	.988
520	.086	.206	.293	.442	.529	.595	.646	.721	.869	.942	.982
522	.085	.206	.294	.442	.526	.591	.645	.725	.866	.945	.984
524	.083	.206	.293	.442	.527	.593	.644	.723	.865	.945	.985
526	.084	.205	.292	.440	.525	.590	.644	.722	.864	.942	.982
527	.084	.206	.293	.440	.525	.589	.645	.723	.862	.942	.984
528	.084	.204	.292	.440	.525	.589	.645	.723	.862	.942	.984
530	.082	.204	.292	.441	.522	.587	.641	.720	.858	.938	.978
532	.083	.204	.291	.441	.516	.584	.640	.714	.859	.936	.977
534	.082	.203	.289	.439	.519	.582	.640	.714	.856	.934	.977
536	.082	.203	.289	.436	.516	.580	.636	.710	.851	.926	.974
538	.082	.203	.305	.440	.517	.582	.640	.714	.858	.932	.972
540	.081	.204	.292	.438	.518	.579	.637	.712	.857	.935	.989

IV. EQUATIONS FOR CALCULATION OF THE IONIZATION CONSTANT K_b AND pK_b

On the basis of the preceding discussion, a simple reaction may be assumed, in which the yellow (basic) form of the indicator combines, or bonds, with a single hydrogen ion with accompanying change in color from yellow to red (fig. 1). By the law of mass action the apparent ionization constant, K_b, for this reaction [1, 4] is given by

$$K_b=(M_H M_Y/M_R)(f_H f_Y/f_R)=K_c f_H f_Y/f_R, \quad (3)$$

in which M_H, M_Y, and M_R represent, respectively, the molar concentrations of the hydrogen ion, the yellow form, and the red form of the indicator, and K_c is equal to $M_H M_Y/M_R$. The corresponding activity coefficients are represented by f with appropriate subscripts. Substituting $(1-\alpha)/\alpha$ for M_Y/M_R, and writing eq 3 in the usual logarithmic form, we have

$$pK_b=-\log[M_H(1-\alpha)/\alpha]-\log[f_H f_Y/f_R]=pK_c-\log[f_H f_Y/f_R] \quad (4)$$

In the above equation, α is determined from the spectrophotometric data by eq 2 and M_H is identical with the molarity of the acid (assuming complete dissociation of hydrochloric acid and neglecting

TABLE 3.—*Calculation of the* pK_e, *activity coefficients and* pH *of metacresolsulfonphthalein in aqueous hydrochloric acid solutions*

Molar concentration of HCl, [H]	Transmittancy at 527.8 mμ, t	Molar absorption index, k	Fractional ionization of indicator, α	Ratio Y/R, $(1-\alpha)/\alpha$	K_e, $[H]\times(1-\alpha)/\alpha$	pK_e, $-\log_{10}K_e$	Activity coefficients		Calculated pH	
							Spectrophotometric, $\sqrt{f_{n}f_{v-}/f_{n+-}}$	Potentiometric, $\sqrt{f_{H}f_{Cl}}$	Spectrophotometric, pH	Potentiometric, pH [1]
0.000	0.939	2.186	0.000			1.703				
.001	.888	4,146	.044	21.907	0.02191				3.02	3.02
.002	.842	5,954	.084	10.916	.02183	1.661	0.953	0.955	2.71	2.72
.004	.774	8,906	.150	5.682	.02273	1.643	.934	.939	2.42	2.43
.006	.720	11,414	.206	3.866	.02319	1.634	.924	.926	2.26	2.26
.008	.676	13,578	.254	2.941	.02352	1.628	.918	.916	2.13	2.14
.010	.643	15,343	.293	2.412	.02412	1.618	.906	.906	2.04	2.04
.015	.577	19,106	.377	1.654	.02480	1.605	.894	.891	1.87	1.88
.020	.532	21,960	.440	1.271	.02541	1.595	.883	.878	1.75	1.76
.030	.477	25,740	.525	0.906	.02718	1.566	.854	.858	1.59	1.59
.040	.438	28,666	.590	.696	.02782	1.556	.844	.844	1.47	1.47
.050	.408	31,156	.645	.550	.02749	1.561	.849	.832	1.37	1.38
.060	.392	32,581	.677	.477	.02862	1.543	.832	.823	1.30	1.31
.075	.370	34,544	.721	.387	.02906	1.537	.826	.812	1.21	1.22
.100	.347	36,757	.770	.300	.03000	1.523	.813	.798	1.11	1.10
.200	.307	40,984	.864	.157	.03144	1.502	.794	.770	0.80	0.81
.500	.278	44,489	.942	.061	.03067	1.513	.804	.776	.40	.41
1.000	.263	46,350	.984	.027	.02677	1.572				
2.000	.258	47,084	1.000							

[1] Measured pH values obtained by using the hydrogen-electrode and glass-electrode assemblies agreed usually within 0.01 with the calculated pH value.

the low concentration of hydrogen ions from the indicator); hence, pK_c is known from the experimental data. The values of K_c and pK_c are given in table 3, and are shown in figure 6 as a function of the ionic strength, μ, computed on the molar basis. The activity coefficients approach unity by definition as the ionic strength decreases to zero on dilution of the solution. Hence, by extrapolation

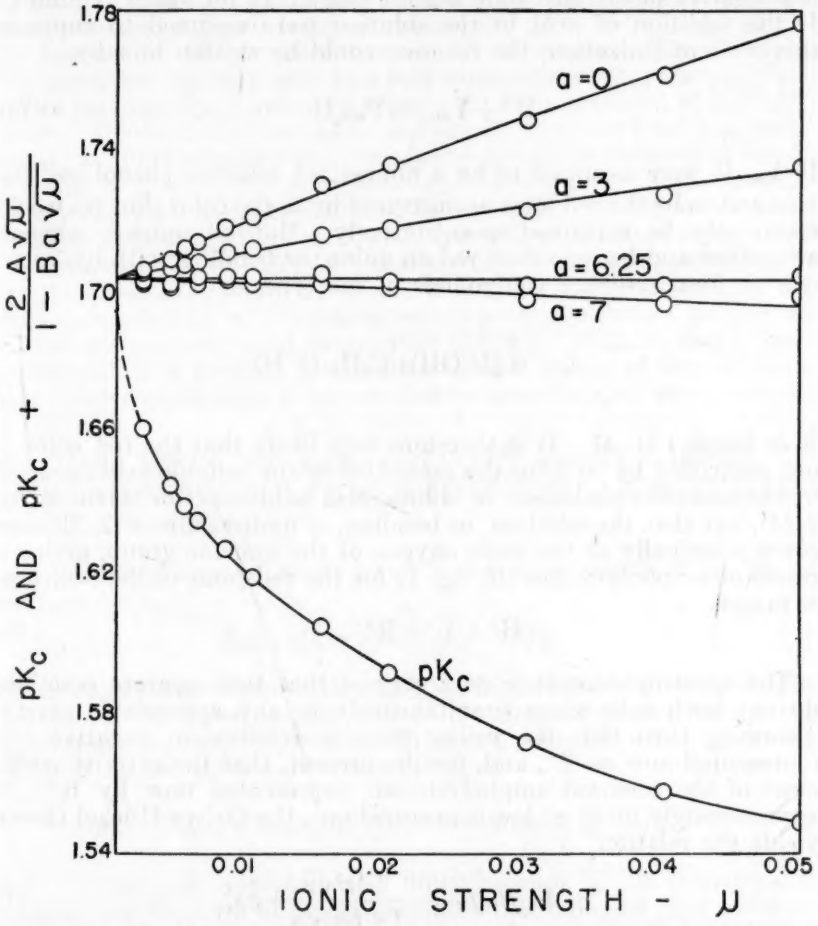

FIGURE 6.—pK_c *values obtained from the spectrophotometric values for metacresolsulfonphthalein in hydrochloric acid at low ionic strengths.*

[1, 5, 6, 8] of the pK_c curve of figure 6 to zero ionic strength the value of pK_b will be obtained. As the slope of pK_c near $\mu=0$ is large and its extrapolation uncertain, this procedure may be greatly facilitated by finding exact or even approximate values for the activity coefficients, such that the function $pK_c - \log(f_H f_Y / f_R)$ is approximately independent of μ and its slope so small that the extrapolation can be made with accuracy (see the other curves in fig. 6). This may be done by use of the Debye-Hückel formula or simplifications thereof for the negatives of the logarithms of the ionic activity coefficients,

when the dimensions of the yellow and red forms of the indicator and proper values z for their electric charges are determined as follows.

There is considerable evidence for the assumption that the sulfonic acids may be regarded as almost completely dissociated in water solution [23] and that the yellow form of metacresolsulfonphthalein is a negative substituted sulfonate ion (see fig. 1), for which z equals 1.[7] If the addition of acid to the solution were assumed to suppress this state of ionization, the reaction could be written broadly

$$H^+ + Y_{SO_3^-} \leftrightarrows Y_{SO_3H}. \tag{5}$$

If Y_{SO_3H} were assumed to be a nonionized quinone phenol sulfonic acid and to be the red form as measured by α, the color changes would apparently be explained quantitatively. But all quinone phenols are yellow and become deep red on union, or bonding, with hydrogen ions to form resonant compounds of the type

$$-(C_6H_4OH)(:C_6H_4:O^+H)$$

R in figure 1 [1, 4]. It is therefore very likely that the red color is not controlled by eq 5 for the ionization of the sulfonic acid group of metacresolsulfonphthalein in dilute acid solutions (or even up to 2 M), but that the addition, or bonding, of hydrogen ions [2, 7] takes place principally at the basic oxygen of the quinone group, giving a resonant ampholytic ion (R, fig. 1) for the red form of the indicator as in eq 6.

$$H^+ + Y^- = R^{+-}, \tag{6}$$

The spectrophotometric data suggest that two separate reactions do not both take place simultaneously to any appreciable extent. Assuming then that the yellow form is a univalent negative ion, represented now as Y^-, and, for the present, that the activity coefficient of the resonant ampholytic ion, represented now by R^{+-}, is approximately unity at low concentrations, the Debye-Hückel theory yields the relation

$$-\log(f_H f_{Y^-}) = \frac{2Az^2\sqrt{\mu}}{1+Ba_1\sqrt{\mu}} + \beta\mu, \tag{7}$$

in which z is unity; A and B have the values 0.5098 and 0.3298 [12], respectively, at 25° C; a_1 is an adjustable parameter used to represent in angstroms the average distance of closest approach of ions; μ is defined as $\sum z_i^2 m_i/2$ as usual; and β is an empirical correction factor. By arbitrarily assigning different reasonable values to a_1, a set of curves is obtained for $pK_c - \log(f_H f_{Y^-}/f_{R^{+-}})$ with small slopes which can be extrapolated accurately, as shown in figure 6. These curves converge at just one pK_b value, 1.703, because at zero concentration and ionic strength of the electrolytes all of the activity coefficients

[7] This is the ionic charge; the contribution of the resonant polar charges ([+] and [−], fig. 1) is disregarded

become unity, and the activity coefficient term of eq 4 becomes zero, regardless of the value of a_i used. K_b is therefore 1.98×10^{-2}.

It should be emphasized at this point that even though a limiting dissociation constant, K_b in this case, is known very precisely, it is not possible to predict from a given α exactly (i. e., to 0.001) what the pH value will be in any mixture of electrolytes. Knowledge of the concentrations of the electrolytes and their valence types, the average values of a_i and β, the dielectric constant, and preferably an independent measure of the activities, are needed to calculate the pH value with precision, and then only by a long series of approximations. This applies particularly to unknown solutions. For a precision of 0.01 pH, however, the computations can be simplified. If $f_{R^{+-}}=1$ holds approximately in dilute solutions and the relation $f_H=f_{Y^-}$ is assumed as usual, eq 4 and 7 give $(pK_b-pK_c)/2=-\log f_H=-\log f_{Y^-}$. The correct average a_i gives a straight pK_c plot through pK_b, and if it is not horizontal its slope is β. With a_i, β, μ, α, and pK_b substituted in eq 4 and 7, the value of pH or $-\log M_H f_H$ can be calculated. An approximately straight horizontal line results, and β may be neglected (see fig. 6) when a_i equals 6.25 A. Extrapolation to $\mu=0$ also gives a pK_b value of 1.703 with an estimated uncertainty of 0.005. With K_b and a_i thus determined, it is possible to calculate the pH values of the solutions from either spectrophotometric or electrometric data, as shown below.

V. COMPARISON OF THE ACTIVITY COEFFICIENTS OF METACRESOLSULFONPHTHALEIN AND HYDROCHLORIC ACID

By rearrangement of terms in eq 3 and substitution of f_{Y^-} for f_Y and $f_{R^{+-}}$ for f_R,

$$f_H f_{Y^-}/f_{R^{+-}}=K_b\alpha/(1-\alpha)M_H. \tag{8}$$

The hydrogen-ion concentration (M_H) is that of the hydrochloric acid and the rest of the right-hand side of the equation is determined entirely from the spectrophotometric measurements, which give the values of K_b and α. From eq 4 is obtained

$$pK_b-pK_c=-\log[f_H f_{Y^-}/f_{R^{+-}}]=-2\log\sqrt{f_H f_{Y^-}/f_{R^{+-}}}. \tag{9}$$

If $f_{R^{+-}}$ is taken as approximately unity because R^{+-} is considered a resonant dipolar form of a nondissociated molecule and f_H is assumed as usual to be equal to f_{Y^-} in the application of the Debye-Hückel equation,

$$(pK_b-pK_c)/2=-\log\sqrt{f_H f_{Y^-}/f_{R^{+-}}}\approx-\log f_H\approx-\log f_{Y^-}, \tag{10}$$

gives an approximate value of f_H or f_{Y^-} listed in column 8, table 3. As the known concentrations of hydrochloric acid are assumed to be equal to M_H, the values of $-\log M_H f_H$ or pH, of all of the solutions of hydrochloric acid and the indicator can be calculated from the spectrophotometric data alone and compared with electrometric

measurements of the pH values. The spectrophotometric pH values are listed in column 10, table 3.

It is important to compare these approximate spectrophotometric activity coefficients and pH values with corresponding ones calculated from the emf data obtained with silver-silver-chloride and hydrogen electrodes in hydrochloric acid solutions by Harned and Ehlers [16]. Their data were computed from eq 11.

$$\frac{(E-E_0)F}{2.3026RT}+\log m_H+\log m_{Cl}=-2\log\sqrt{f_H f_{Cl}}. \quad (11)$$

After reducing their published emf values to activity coefficients on a molarity basis, a curve was drawn for $\sqrt{f_H f_{Cl}}$ as a function of $\sqrt{\mu}$, from which values of $\sqrt{f_H f_{Cl}}$ were read which corresponded to the concentrations of hydrochloric acid used in the spectrophotometric work, as shown in column 9, table 3. The right side of eq 11 is obtained from the electrometric methods and is analogous to the right side of eq 9 for the spectrophotometric work. Since f_H is the same in both cases, it follows that f_{Cl} is to be compared with $f_{Y^-}/f_{R^{+-}}$. If $f_H=f_{Cl}=\sqrt{f_H f_{Cl}}$ as usually assumed, then the products of the $\sqrt{f_H f_{Cl}}$ and the corresponding M_H (columns 1 and 9) are the hydrogen-ion activities ($M_H f_H$) whose negatives of their common logarithms are the electrometric pH values (column 11). The spectrophotometric activity coefficients ($f_{Y^-}/f_{R^{+-}}$) and electrometric activity coefficients (f_{Cl}) agree well up to 0.05 M hydrocholoric acid and even better if the listed experimental values of $\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$ are plotted to obtain a smooth curve from which values may be read for comparison with the smooth curve data listed for $\sqrt{f_H f_{Cl}}$. Above 0.05 M hydrochloric acid, however, the $\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$ data gradually rise above those for $\sqrt{f_H f_{Cl}}$, and probably for the same reasons that cause a similar rise in mixtures of indicator, hydrochloric acid, and salts discussed below; namely, a decrease of $f_{R^{+-}}$ below unity.

VI. ACTIVITY COEFFICIENTS OF METACRESOLSULFONPHTHALEIN AND 0.01-*M* HYDROCHLORIC ACID IN THE PRESENCE OF SALTS

It has long been known that addition of pure neutral salts to solutions of indicators in dilute acid or alkali causes a normal change in activity coefficients and hence in pH and color. There may be also a specific or abnormal [1, 8] salt effect characterized by a definite change in hue arising from a shift in the absorption band with respect to wave number and accompanied by changes in absorption index. Spectral transmittancy curves were therefore obtained for 1.25×10^{-5} M metacresolsulfonphthalein mixed with 0.01 M hydrochloric acid and the molar concentrations of potassium chloride, strontium chloride, and barium chloride shown in column 1 of table 4. The transmittancy of each mixture at 527.$_5\mu$ is given in column 2. The calculation of the spectrophotometric and electrometric activity coefficients and pH values are made by use of eq 4, 9, and 11; 1.703 for pK_b; and values of α obtained from the transmittancy data in column 2, table 4. The

spectrophotometric activity coefficients are given in column 3, table 4.

TABLE 4.—*Effects of salts upon the transformation of metacresolsulfonphthalein* (1.25×10^{-5} *M*) *in 0.01 M hydrochloric acid*

Concentration of salt in 0.01 *M* HCl	Transmittancy of solution at 527.4 mμ, *t*	Activity coefficient [a]		Calculated pH		Measured pH	
		Spectrophotometric, $\sqrt{f_H f_{Y^-} f_{R^{+-}}}$	Potentiometric, $\sqrt{f_H f_{Cl}}$	Spectrophotometric data	Potentiometric data	Hydrogen electrode	Glass electrode
POTASSIUM CHLORIDE							
0.01	0.659	0.870	0.873	2.06	2.06	2.06	2.05
.02	.666	.852	.851	2.07	2.07	2.06	2.05
.05	.674	.832	.816	2.08	2.09	2.07	2.06
.10	.686	.802	.787	2.10	2.10	2.07	2.08
.50	.695	.780	.715	2.10	2.15	2.07	2.07
.72	.685	.805	.720	2.10	2.14	2.05	2.05
1.27	.663	.861	.762	2.06	2.12	2.00	1.99
1.71	.647	.902	.802	2.04	2.10	1.95	1.96
2.01	.621	.974	.835	2.01	2.08	1.93	1.92
3.42	.530	1.268	1.035	1.90	1.99	1.70	1.69
BARIUM CHLORIDE							
0.01	0.668	0.848	0.840	2.07	2.08	2.05	2.07
.04	.687	.795	.772	2.10	2.11	2.05	2.06
.06	.697	.775	.752	2.11	2.12	2.06	2.06
.10	.701	.763	.730	2.11	2.14	2.05	2.04
.20	.706	.754	.706	2.12	2.15	2.03	2.01
.25	.701	.760	.703	2.11	2.15	2.01	2.00
.36	.696	.781	.710	2.11	2.15	1.97	1.96
.50	.679	.820	.729	2.09	2.14	1.92	1.90
.80	.648	.901	.795	2.05	2.10	1.80	1.78
1.00	.631	.975	.853	2.04	2.07	1.74	1.72
1.12	.602	1.027	.902	1.99	2.05	(b)	1.66
STRONTIUM CHLORIDE							
0.01	0.665	0.854	0.835	2.07	2.08	2.08	2.06
.05	.686	.802	.761	2.10	2.12	2.08	1.96
.10	.696	.778	.729	2.11	2.14	2.08	1.82
.30	.696	.779	.713	2.11	2.15	1.99	1.88
.50	.678	.815	.738	2.09	2.13	1.90	1.87
.70	.656	.877	.799	2.06	2.09	1.82	1.79
.80	.644	.910	.838	2.04	2.08	1.78	1.73
2.00	.468	1.538	1.633	1.81	1.79	(b)	1.00
2.36	.413	1.885	[c] 2.016	1.72	1.70	(b)	.88

[a] These activity coefficients were obtained from the data of Harned and Hamer [14] for KCl, Harned and Geary [15] for $BaCl_2$ and Vance [16] for $SrCl_2$. Their data were corrected from a molal to a molar basis. See footnote 8.

[b] Measurements could not be made with the hydrogen-electrode assembly owing to diffusion of the salt and acid solutions through the saturated KCl solution.

[c] Estimated.

At 0.2 to 0.5 *M* salt concentrations these transmittancies go through maxima, and the corresponding absorption indices and activity coefficients therefore go through minima. Harned, Hamer, Geary, Vance, and Ehlers [14, 15, 16, 17] showed by the use of emf methods that the mean electrometric activity coefficients, $\sqrt{f_H f_{Cl}}$, of 0.01 *M* hydrochloric acid go through minima when mixed with approximately the same concentrations of the three salts used in this work. After expressing the molality of each salt in terms of its corresponding molarity,[8] the emf data were used to calculate the activity coefficients

[8] To obtain the molarities (M) from the molalities (m), the following equations were used (Hamer, unpublished):

KCl: $M=0.99707m-0.028100m^{3/2}+0.0001412m^3$; $BaCl_2$: $M=0.99707m-0.026042m^{3/2}-0.003452m^3$; $SrCl_2$: $M=0.99707m-0.019773m^{3/2}-0.0027680m^3$; then $f_M=0.99707mf_m/M$.

on the molar basis. The mean activity coefficients (molar basis) were then plotted as a function of the molar concentrations of the salts. The values of $\sqrt{f_H f_{Cl}}$ which corresponded to the molar concentrations of the salts used in the spectrophotometric work were then read from the curves and are given in column 4, table 4.

A comparison of columns 3 and 4 of table 4 shows that the mean spectrophotometric activity coefficients, $\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$, are in general larger than the coefficients calculated from the electrometric data for $\sqrt{f_H f_{Cl}}$. Since f_H is the same in both methods for the given concentration of salt, it follows that $f_{Y^-}/f_{R^{+-}}$ must be larger than f_{Cl}. The difficulty in ascribing definite values to f_{Y^-} and $f_{R^{+-}}$ arises from the unknown contribution of their resonant dipolar states ([+] and [−] in fig. 1) to the values of z and the activity coefficients. The yellow form will be assigned tentatively $z=1$ for the following reasons: (1) The work on the dipole moments of benzeins [7], whose quinone-phenol chromophores are identical with those of Y^-, shows that the concentration of the resonant dipolar form is only a few percent of that of the ionic form (e. g., Y^- without [+] and [−] charges). (2) The resonant dipole structure of R^{+-} does not make $f_{R^{+-}}$ fall much below unity (see columns 4, 8, 12, 16 in table 5). Hence a few percent of the dipolar form of Y^- (e. g., Y^{-+-}, fig. 1) would produce only a minor effect on the over-all $-\log f(Y^- + Y^{-+-})$. In any event, the effects of the dipole contributions are somewhat compensated in the ratio $f_{Y^-}/f_{R^{+-}}$.

If use is now made provisionally of the hypothesis of Lewis and Randall [18] that the activity coefficient of any univalent ion in dilute aqueous solution depends only upon the ionic strength of the solution, a hypothesis that is also inherent in the Debye-Hückel theory of dilute mixed electrolytes, the activity coefficients of the chloride and single-charged indicator ions would be approximately the same. Hence if we place f_{Cl} equal to f_{Y^-}, we must get $f_{R^{+-}}$ and $\sqrt{f_{R^{+-}}}$ values appreciably less than unity, as shown in columns 4, 8, 12, 16, table 5. An expression developed by Kirkwood [19] for the activity coefficient of a fixed dipole (ampholyte) also gives values less than unity, which is in harmony with the present experimental evidence that the resonant dipolar red salt should not be treated as an uncharged molecule in hydrochloric acid or its mixtures with salts. Furthermore, the specific salt effects characterized by the shifts of the absorption bands (fig. 5), discussed above, are also being taken into account in the final corrections of α required for correct application of eq 4 to determine the pK_b and pH values for these acid-salt-indicator mixtures.

A definite departure from unity of the activity coefficients for the red form of the indicator may be taken as further evidence, supported by organic structural relations discussed on page 324, for the assumption that the reaction is expressed by eq 6 for a resonant ampholyte, rather than by eq 5, in which the red form would be an uncharged molecule and have an activity coefficient probably more nearly unity.

As this article is limited to comparisons of the approximate pH values obtained by the spectrophotometric and electrometric methods,

the data of table 4 may be treated as follows: The very small effect of $-\log f_{R^{+-}}$ will be disregarded and the approximate pH values, $-\log (M_H f_H)$, of 0.01 M hydrochloric acid in the presence of salts obtained by adding to 2 (i.e., $-\log 0.01$) the values of $-\log\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$ (computed from column 3, table 4) and those of $-\log\sqrt{f_H f_{Cl}}$ (computed from column 4, table 4) to get the "spectrophotometric" and "potentiometric" pH data, respectively. These pH values are given in columns 5 and 6, table 4. The agreement is within approximately 0.05 pH unit in all cases, even including the most concentrated solutions. For the 30 solutions listed, however, the average spectrophotometric pH values are about 0.03 less than the electrometric pH values of the acid-salt solutions.

Since the pH determined by spectrophotometric measurements is lower than that obtained by electrometric measurements, and $f_{Y^-}/f_{R^{+-}}$ values are larger than f_{Cl} for all the solutions studied, the next step is to attempt adjustments of f_{Cl}, f_{Y^-}, and $f_{R^{+-}}$ to give the same spectrophotometric and electrometric pH values. If $f_{Cl}=f_{Y^-}$ and $\mathrm{pH}=-\log(m_H\sqrt{f_H f_{Cl}})=-\log(m_H\sqrt{f_H f_{Y^-}})$ then the practical use of $\mathrm{pH}=-\log(m_H\sqrt{f_H f_{Y^-}/f_{R^{+-}}})=-\log(m_H\sqrt{f_H f_{Y^-}})+\log\sqrt{f_{R^{+-}}}$ will give spectrophotometric pH values too low by $\log\sqrt{f_{R^{+-}}}$. The values for $\sqrt{f_{R^{+-}}}$ are obtained by dividing $\sqrt{f_H f_{Cl}}$ by $\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$ at the same ionic strength and are given in columns 4, 8, 12, and 16 of table 5. The first result is that the deviation of $\sqrt{f_{R^{+-}}}$ from unity is small in comparison with the corresponding differences between unity and $\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$ and $\sqrt{f_H f_{Cl}}$, and that the contributions of the $-\log\sqrt{f_{R^{+-}}}$ values (columns 5, 9, 13, 17 of table 5) to the pH for the four solutions, even though differing somewhat among themselves, are small in comparison with $-\log\sqrt{f_H f_{Cl}}$ (and hence $-\log\sqrt{f_H f_{Y^-}}$). For the 30 solutions listed in table 4, the average spectrophotometric pH values are about 0.03 less than the electrometric pH values. The average correction for the $-\log\sqrt{f_{R^{+-}}}$ for the same solutions is +0.03 pH, which therefore makes the average spectrophotometric pH values practically the same as the electrometric pH values. Similar corrections for the $-\log\sqrt{f_{R^{+-}}}$ for the hydrochloric acid solutions in table 3 make the average pH values of column 10 practically the same as those of column 11. The second result is therefore that there is still some doubt whether f_{Cl} and f_{Y^-} are absolutely equal, in view of the polar nature of the latter, and whether either or both may have slightly different values in the solutions of different electrolytes of equal ionic strength. This question also applies to buffers. The uncertainties from the above cause, in the pH values are less than 0.05 pH in solutions up to unit ionic strength.

The pH values of these solutions were also measured with saturated calomel half-cells and hydrogen and glass electrodes, in a room controlled at 25° C, to determine the pH errors which may be encountered with routine apparatus. The value 0.24503 volt was assigned to the saturated calomel electrode with the liquid-junction potential by calibration with potassuim acid phthalate. For the 27 values listed in column 7, table 4, the average results obtained with the glass electrode are 0.027 pH lower than those with the hydrogen electrode.

TABLE 5.—*Comparison of the activity coefficients of metacresolsulfonphthalein in in 0.01 M hydrochloric acid*

Ionic strength (molar)	Hydrochloric acid				Potassium chloride in 0.01 *M* hydrochloric acid			
	Activity coefficients				Activity coefficients			
	Spectrophotometric $\sqrt{f_H f_Y^- / f_R^{+-}}$	Potentiometric $\sqrt{f_H f_{Cl}}$	$\frac{\sqrt{f_H f_{Cl}}}{\sqrt{f_H f_Y^- / f_R^{+-}}}$	$-\log \sqrt{f_R^{+-}}$	Spectrophotometric $\sqrt{f_H f_Y^- / f_R^{+-}}$	Potentiometric $\sqrt{f_H f_{Cl}}$	$\frac{\sqrt{f_H f_{Cl}}}{\sqrt{f_H f_Y^- / f_R^{+-}}}$	$-\log \sqrt{f_R^{+-}}$
0.01	0.906	0.906	1.000	0.000	0.906	0.906	1.000	0.000
.02	.878	.878	1.000	.000	.873	.873	1.000	.000
.03	.863	.857	.993	.003	.856	.851	.994	.003
.04	.852	.844	.991	.004	.845	.836	.989	.005
.05	.842	.832	.988	.005	.835	.825	.988	.005
.06	.835	.824	.987	.006	.828	.816	.986	.006
.08	.823	.809	.983	.007	.816	.802	.983	.007
.10	.815	.799	.980	.009	.807	.791	.980	.008
.20	.796	.770	.967	.015	.787	.754	.958	.019
.50	.806	.776	.963	.016	.781	.715	.915	.038
1.00	.860	.825	.959	.018	.820	.730	.890	.050
2.00	----------	----------	----------	----------	.946	.837	.885	.053
3.00	----------	----------	----------	----------	1.140	.970	.851	.070

A comparison of the measured pH values (columns 7 and 8, table 4) with the calculated pH values (columns 5 and 6, table 4) throws some light on the errors likely to be encountered in routine pH measurements of fairly concentrated solutions of salts and acids with cells involving a liquid-junction potential of unknown value, for which no correction is attempted. The values in column 6 do not involve a liquid-junction potential, whereas those in columns 7 and 8 were obtained with cells having a liquid-junction between the saturated calomel half-cell and the salt-acid solution. For solutions of 0.01 *M* hydrochloric acid and not over 0.05 *M* salt, the agreement is generally of the order of 0.05 pH, but for the concentrated solutions, discrepancies of 0.3 to 0.4 unit are observed, the results being somewhat erratic because of the difficulty in establishing sharp liquid junctions. In an article recently published [20] caution was recommended against undue optimism in assigning pH values to within 0.05 pH in cases such as the above when liquid junctions are formed between electrolytes of widely different valance types, concentrations, and ionic mobilities. When the pH values of acid or acid-salt solutions of the types reported here are obtained by spectrophotometric and by electrometric measurements without liquid junctions, the average agreement is within about ± 0.05 pH unit in even fairly concentrated solutions.

hydrochloric acid, and in potassium chloride, barium chloride and strontium chloride at the same ionic strengths

Barium chloride in 0.01 *M* hydrochloric acid				Strontium chloride in 0.01 *M* hydrochloric acid			
Activity coefficients				Activity coefficients			
Spectrophotometric $\sqrt{f_H f_Y^- / f_{R^+}}$	Potentiometric $\sqrt{f_H f_{Cl}}$	$\frac{\sqrt{f_H f_{Cl}}}{\sqrt{f_H f_Y^- / f_{R^+}}}$	$-\log \sqrt{f_{R^+}}$	Spectrophotometric $\sqrt{f_H f_Y^- / f_{R^+}}$	Potentiometric $\sqrt{f_H f_{Cl}}$	$\frac{\sqrt{f_H f_{Cl}}}{\sqrt{f_H f_Y^- / f_{R^+}}}$	$-\log \sqrt{f_{R^+}}$
0.906	0.906	1.000	0.000	0.906	0.906	1.000	0.000
.878	.876	.998	.001	.883	.881	.998	.001
.861	.855	.993	.003	.866	.861	.994	.003
.848	.839	.989	.005	.854	.847	.992	.003
.837	.827	.988	.005	.846	.834	.986	.006
.829	.817	.986	.006	.839	.825	.983	.007
.815	.800	.982	.008	.828	.807	.975	.011
.804	.788	.980	.009	.820	.794	.968	.014
.776	.749	.965	.015	.793	.754	.951	.022
.755	.709	.939	.027	.769	.714	.928	.032
.770	.706	.917	.038	.783	.719	.918	.037
.860	.761	.885	.053	.864	.788	.912	.040
.970	.858	.884	.053	.980	.912	.931	.031

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WASHINGTON, August, 23, 1943.

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